DRAFT

ALBERTA AMBIENT AIR QUALITY GUIDELINES

ETHYLENE
(INTERIM GUIDELINES)

June 1997

Standards and Guidelines Branch
Environmental Assessment Division
Alberta Environmental Protection

The interim air quality guidelines derived in this document protect vegetation from adverse effects resulting from ethylene exposure. This guideline is based on a thorough evaluation of available scientific information.

This document has been reviewed within Alberta Environmental Protection. However, we recognize that other information may exist that could have a bearing on this document. For this reason alone, this document is called "DRAFT". Comments from the public and other stakeholders are invited until June 1, 1998. After this period, the comments will be addressed in a "Final" document.

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EXECUTIVE SUMMARY

Ethylene is produced at low levels by vegetation, and is therefore a naturally occurring compound in ambient air. Ethylene is also produced by combustion in forest and grass fires. The concentration in ambient air resulting from these natural sources is typically low, approximating 10 µg m^{-3} (equal to 12 parts per billion) Combustion of fossil fuels, and processing of natural gas in petrochemical facilities (e.g. production of plastics) result in emissions which may substantially increase ambient air ethylene concentrations. As ethylene is known to affect vegetation at low levels, there is the potential for ethylene to affect Alberta vegetation.

In Alberta, guidelines are based upon a review of the scientific literature ("criteria"). A guideline may take the form of a numerical concentration, value, or narrative statement which is intended to prevent deterioration of air quality. This document provides a review of the available scientific data regarding ethylene effects, and based on this review, an interim guideline for ethylene for each of two averaging periods is derived.

ALBERTA AMBIENT AIR ETHYLENE GUIDELINES (INTERIM)

Interim Ethylene Guideline	Averaging Period	Daytime Application Period	Seasonal Application Period
120 µg m$^{-3\dagger}$	6 hours	0300 to 2200 hours	May 1 through September 30, inclusive
50 µg m^{-3}	30 days	0300 to 2200 hours	May 1 through September 30, inclusive

† This is the preliminary guideline currently used in Alberta.

As ethylene affects vegetation at levels several orders of magnitude lower than levels affecting humans and animals, the focus of this review is on the establishment of interim ethylene guidelines for the protection of vegetation. It therefore follows that these guidelines are protective in terms of human health.

This is the first comprehensive analysis of ethylene emissions and effects in Alberta. In the past, to assess the potential effects of ethylene from sources present in the province, guidelines in effect in other jurisdictions have been evaluated for use. The Ontario guideline (120 µg m^{-3}, 6-hour running average) was found to be the most stringent, and has therefore been used in Alberta on a preliminary basis. The present review and evaluation of the scientific criteria supports the continued use of this guideline on an interim basis.

The 6-hour (120 µg m^{-3}) guideline strives to protect vegetation from short-term exposures to ethylene in air. However, the data presented in the scientific literature indicate that long-term exposure to a lower concentration of ethylene may also be detrimental. To ensure that vegetation is not adversely affected by long-term low-level exposures, an interim ethylene guideline of 50 µg m^{-3} (30-day running average) is proposed.

Since vegetation is active primarily during a summer growing season, these interim guidelines are to be applied during the period of May 1 through September 30, inclusive. Both interim guidelines are to be applied only between 0300 hr (3:00 a.m.) and 2200 hr (10:00 p.m.), the period when plants are presumed to be sensitive to ethylene exposure.

Uncertainties remain regarding the effects of ethylene on vegetation. It is recommended that these levels, averaging periods, and application of the guidelines be reevaluated as additional information becomes available. Additional scientific data will be available following the completion of research conducted under environmental conditions and ethylene levels expected to occur in Alberta.

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1.0 INTRODUCTION

Ethylene is emitted into the atmosphere from a number of natural and anthropogenic sources. It is a potent regulator of plant growth and development and may have substantial effects at low concentrations in ambient air. With the knowledge that ethylene is being emitted into our atmosphere, and that ethylene at low concentrations may affect plant growth and development, the need for an ethylene air quality guideline based on the analysis and evaluation of the scientific literature has become apparent. This document provides this review and analysis.

The possible adverse health effects associated with human exposure to ethylene are not discussed in this document. For a review of literature pertaining to the health effects of ethylene, see the National Research Council of Canada (1985) publication.

At present, Alberta does not have a protocol for the development of ambient air quality objectives and guidelines. Alberta Environmental Protection has been participating in the development of a protocol for the development of national ambient air quality guidelines and objectives (Canadian Environmental Protection Act; Federal-Provincial Advisory Committee, 1996). At present the national protocol is in draft form only, and may undergo further changes before it is available for routine use. However, in the absence of a protocol for the development of Alberta ambient air quality objectives and guidelines, the draft national protocol has been used as a guide for the development of Alberta ambient air quality guidelines for ethylene.

Alberta Ambient Air Quality Guidelines are based on an evaluation of the scientific literature. This document presents a summary and evaluation of the scientific literature regarding sources, ambient ethylene levels in rural, industrial and urban settings, and potential environmental effects of ethylene. This critical evaluation provides the foundation for proposing that an ethylene guideline for each of two averaging periods be implemented on an interim basis. In the preparation of this document, all available studies documenting the response of an environmental receptor (primarily plants and microorganisms) were evaluated for their applicability in the derivation of the ambient air quality guidelines for ethylene. Many studies were not relevant, and were rejected. The most common reasons for rejection were that inappropriate concentrations of ethylene were used in the study (usually too high), the type of exposure system used was so different from typical ambient exposures so as to make the results impossible to interpret in the context of air quality, or presentation and statistical treatment of the data was not acceptable. Studies which provide useful information are described in the text of this document. Studies which yield no information relevant to air quality or receptor response, or are not helpful in the development of the ethylene guideline are not discussed in the body of the document. These rejected studies are listed in the final section (Section 13.0, Literature Not Cited).

Molecular Formula	C_2H_4	Molecular Weight (g mole^{-1})	28.05
CAS Number	74-85-1	OHM-TADS Number	7216713
STCC Number	4905734	UN Numbers — Ethylene Gas — Ethylene Liquid	1962 1038
Melting Point (°C)	-169.2	Boiling Point (°C)	-103.7
Specific Gravity (at -104.0°C)	0.566	Solubility in Water (mg l^{-1}; at 0°C)	131
Vapour Density (at 25°C)	0.978	Odour Threshold (mg m^{-3})	10^2 to 10^3
Log$_{10}$ Octanol:Water Partition Coefficient[††]			1.13

[†] Verschueren (1983)
[††] Stahl (1969; cited in National Research Council, 1985)

2.0 PHYSICAL AND CHEMICAL CHARACTERISTICS OF ETHYLENE

2.1 Physical and Chemical Characteristics, Registry Numbers

Synonyms for ethylene include ethene, bicarburretted hydrogen, Elayl, and olefiant gas. The physical and chemical characteristics, and the various registry numbers, for ethylene are presented in Table I.

2.2 Conversion Factors Used in this Review

There is a wide diversity of units of concentration used in the scientific literature. The concentration of ethylene in air may be expressed on a volume to volume (v/v), weight to volume (w/v), or weight to weight (w/w) basis. The familiar units of parts per million (ppm) and parts per billion (ppb) are measures in v/v; that is 1 ppm of ethylene is the concentration resulting from the presence of 1 µl of ethylene in a total volume of 1 litre (1,000,000 µl). Parts per billion is a concentration 1000-fold lower than ppm, and parts per trillion is a 1000-fold lower concentration than ppb.

Occasionally, concentrations of organic gases are expressed on the basis of the concentration of carbon in air. Examples include ppbC (parts per billion carbon) and pptC. Since ethylene contains 2 carbon atoms, the concentration of 1 ppm ethylene is equivalent to 2 ppm carbon (2 ppmC), assuming the absence of other carbon-containing gases.

In Alberta guidelines, air contaminant concentrations are expressed in the units of µg m^{-3}. This is an expression in terms of weight to volume (w/v). In this document, all concentrations presented in original references have been converted using the following conversion factors:

1 ppm = 1,150 µg m^{-3} 1 ppbC = 0.575 µg m^{-3}
1 ppb = 1.15 µg m^{-3} 1 pptv = 0.00115 µg m^{-3}

$$1 \; \mu l \; l^{-1} = 1{,}150 \; \mu g \; m^{-3} \qquad \qquad 1 \; Pa = 11{,}350 \; \mu g \; m^{-3}$$

In the sections of this document which discuss concentrations of ethylene in water, concentrations are expressed in micrograms per litre of water ($\mu g \; l^{-1}$), or in the cases of very low concentrations, as nanograms per litre ($ng \; l^{-1}$).

3.0 IDENTIFICATION AND CHARACTERIZATION OF ETHYLENE SOURCES

Ethylene is produced naturally by microbes and plants. Ethylene is also produced from combustion of organic compounds, both in natural processes (e.g. forest fires) and as a result of human activity (fossil fuel combustion, processing of natural gas). In plants, ethylene functions as a plant hormone, and affects growth and development at concentrations 100 to 1,000,000 times lower than other hydrocarbons (Abeles, 1973). Plants respond to environmental variations and stresses by modulating both the production and response to ethylene.

On a global scale, it has been estimated that 18 to 45 $\cdot$ 10^6 tonnes are released annually into the atmosphere (Sawada and Totsuka, 1986), of which 74% is attributed to natural sources and 26% to anthropogenic sources. Of the anthropogenic portion, 77% is attributed to biomass burning, while 21% is attributed to the burning of fossil fuels (Sawada and Totsuka, 1986).

3.1 Natural Production of Ethylene

3.1.1 Soil Microorganisms

Ethylene is produced in the soil as a by-product of microbial (bacterial and fungal) degradation of organic matter, and by synthesis within the microbes as a result of normal metabolic activity. The metabolic pathways of microbial ethylene production have been described by Bird and Lynch (1974) and Primrose (1979).

Only a subset of the total complement of soil bacteria and fungi are capable of producing ethylene (DaSilva *et al.*, 1974; Cook and Smith, 1977; Sutherland and Cook, 1980), however, soil microbes in a wide variety of ecosystems are capable of producing ethylene (e.g. microbes within southeastern coastal plain and coniferous forest soils). The O-horizon (the upper soil layer, high in organic matter content) of forest soils in Finland was found to release up to 0.001 μg cm^{-3} (soil) hr^{-1} (Weber *et al.*, 1983). Ethylene production in soil varies in response to a wide number of environmental variables, including temperature, soil moisture content, organic matter content, soil amendments (e.g. manure), compaction, and oxygen content (Burford, 1975; Cook and Smith, 1977; Campbell and Moreau, 1979; Lindberg *et al.*, 1979; Lynch and Harper, 1980). Anaerobic conditions (<2% oxygen) in the soil resulted in an increase in the amount of ethylene present in the soil; this ethylene was the result of microbial action (Smith and Restall, 1971; Sexstone and Mains, 1990). As a result of this environmental variability, microbial synthesis of ethylene varies naturally within the ecosystem. Physiologically active levels of ethylene may accumulate naturally in coniferous forest soils, where they affect both tree root and microbial (fungal) growth (Lindberg *et al.*, 1979).

3.1.2 Higher Plants

The biosynthetic pathway of ethylene production in plants is now well understood, and is presented in detail by Abeles *et al.* (1992) and Imaseki (1991). Ethylene production is regulated at a number of metabolic steps, such that increases or decreases in production are controlled in a strict fashion in response to environmental signals. Stress, such as flooding, wind or other

mechanical bending (e.g. lodging), wounding (mechanical and pathogenic attack), and chemical exposure (e.g. ozone), tends to increase ethylene production (Abeles, 1982; Hyodo, 1991; Mattoo and White, 1991). Elevated CO_2 levels also promote ethylene biosynthesis in plants (Finlayson and Reid, 1994; Grodinski, 1992). As global CO_2 levels rise, ambient, background ethylene levels may also rise, and this may affect vegetation on local, regional and global scales.

In some plant species, ethylene emissions increase during the day, and decrease at night (El-Beltagy and Hall, 1974; Voesenek et al., 1990), while in others, ethylene emissions are constant throughout the day (Foster et al., 1992). Rates of synthesis vary by species, tissue type (e.g. leaf, flower) and age of the plant. As a hormone, synthesis (and hence release) of ethylene is often initiated in order to stimulate a naturally occurring process. Fruit ripening (climacteric ethylene synthesis and release) is the classic example of this process (reviewed in Abeles et al., 1992). Emissions from several hard and soft wood species in dry and swamp areas of Louisiana ranged from below the detection limits (ca. 10 mg kg^{-1} hr^{-1}) to 30 mg kg^{-1} hr^{-1}, which resulted in ambient air background levels of 0.4 to 0.5 µg m^{-3} (Khalil and Rasmussen, 1992).

3.1.3   Algae and Lichens

The unicellular green alga *Haematococcus pluvialis* has been found to produce ethylene, although an enzymatic complex different from that present in higher plants was apparently used (Maillard et al., 1993). *Acetabularia mediterranea* algae also produces ethylene, possibly by the same biosynthetic pathway as in higher plants (Kevers et al., 1986).

Lichens with both eukaryotic and prokaryotic photobionts were found to naturally produce ethylene (Ott and Zwoch, 1992). Lichen samples were obtained from south Sweden, the maritime Antarctic and western Germany, and represented eight species. As with the unicellular alga, enzymes apparently different from those present in higher plants were involved in ethylene biosynthesis. Lurie and Garty (1991) concluded that the lichen *Ramalina duriaei* produces ethylene using the same precursors as in plants, but with different enzymes. Thus, although ethylene biosynthesis and release appears to occur in a wide range of plants, algae and lichens, differences in the mechanisms of production are apparent.

3.1.4 Animals and Humans

Mammalian production of ethylene is low, and has been observed in only a limited number of studies. A 3- to 4-fold increase in ethylene content of exhaled air from 3 non-smoking subjects relative to inhaled room air (7.9 µg m^{-3}) was observed by Ram Chandra and Spencer (1963). This was a very small, limited study. Ethylene in expired air was substantially higher from a smoker (120 µg hr^{-1}) than from a non-smoker (0.91 µg hr^{-1}) (Conkle et al., 1975). There is insufficient data available with which to evaluate the contribution to the atmospheric pool from these natural sources. However, it is likely low relative to microbial and vegetative sources.

3.1.5 Other Natural Ethylene Sources

Ethylene is released into the atmosphere during volcanic activity (Stoiber et al., 1971),

however, annual global volcanic ethylene emissions have not been quantified. Smoke from forest fires contains ethylene, however, the amount of ethylene generated annually from fires of natural causes is unknown. Generation of ethylene from fires of human origin is discussed below (Section 4.2.1, *Combustion*).

The rate of release of ethylene from the north Atlantic ocean was estimated to be 6×10^{-11} g cm^{-2} h^{-1} (Rudolph and Ehhalt, 1981). Atmospheric removal was estimated at 9×10^{-11} g cm^{-2} h^{-1}; these estimates suggest that a concentration of 5.5 µg l^{-1} ethylene is present in the north Atlantic (Rudolph and Ehhalt, 1981). In an earlier study, ethylene concentrations in the Gulf of Mexico, Caribbean Sea, Atlantic Ocean, and Pacific Ocean, were found to range from 0.5 to 8.3 µg l^{-1} (Swinnerton and Lamontagne, 1974). The variation in concentrations among sample sites appeared to be a consequence of biological activity rather than environmental contamination.

Ethylene is produced biotically and abiotically in estuarine environments, with higher concentrations found in areas with high primary productivity (Lee and Baker, 1992). Ethylene concentrations in samples obtained from the Skidaway River (an estuarine river) near Savannah GA averaged 0.01 µg l^{-1}, which increased to 0.04 µg l^{-1} following an 8-hour exposure to sunlight. Similar processes may occur in Alberta's aquatic systems, however, these are undocumented.

3.2 Anthropogenic Production of Ethylene

3.2.1 Combustion

Burning of agricultural field residues and forests contributes to atmospheric ethylene levels. While burning of agricultural wastes is becoming a less common practice, ethylene levels within the smoke from these fires is substantial. Combustion of wheat straw in a closed warehouse (a volume of 3,190 m^3) produced 0.2 g C_2H_4 kg^{-1} of straw (Gerakis *et al.*, 1978). Darley *et al.* (1966) reported that the combustion of wood chips generated 1.1 g kg^{-1}, while combustion of green brush resulted in the generation of 1.3 g kg^{-1} of brush burned, 1.1 g kg^{-1} of barley straw burned, and 0.4 g kg^{-1} of native (Californian) brush burned. Boubel *et al.* (1969) found that 0.8 g kg^{-1} was produced from grass and straw stubble burned under laboratory conditions. Levels of ethylene in the air were elevated near (10 m) the flame front of a burning wheat stubble field (total area 20,000 m^2), however, levels diminished rapidly such that 30 m from the flame front ethylene levels were not above pre-burn concentrations (Gerakis *et al.*, 1978). One hour after burning ceased, the level of ethylene in the air space of soil cracks was elevated (2,185 µg m^{-3}). This concentration is sufficient to affect plant root growth and development. Rapid diffusion and dilution of ethylene produced by burning stubble in smaller fields rapidly reduces air ethylene levels to background. Ambient levels would be expected to be higher in regions in which larger scale burning takes place.

Burning of agricultural wastes in Japan was investigated as a possible source of ground-level ethylene (Sawada, 1985). A concentration of 1.3 µg m^{-3} was observed at 1,200 m above ground level, increasing to 89 µg m^{-3} 1.2 m above the burning paddy fields. However, since the burning only occurs during a 4- to 5-day period in the afternoon and night in late October, Sawada (1985) suggested that these levels do not invoke significant responses by exposed plants.

Forest fires (both wildfires and managed burnings) also contribute to atmospheric ethylene levels. Sawada and Totsuka (1986) have estimated that burning of tropical rain forests is the single largest anthropogenic source of global atmospheric ethylene (20% of total anthropogenic emissions). Abeles (1982) suggests an average of 1 kg ethylene is produced per tonne of burned vegetation in the United States. Yamate (e1974; cited in Abeles, 1982) estimates that the total contribution of ethylene from burning vegetation at 80×10^3 tonnes per year in the United States. More ethylene is released from burning vegetation during the smoldering phase (following peak fire activity). Application of flame retardant chemicals enhances ethylene emissions, possibly by lowering fire temperature and extending the length of the smoldering phase of the fire (Sandberg et al., 1975). Smoldering wood, needles and litter produce more ethylene (up to 5 g kg^{-1}) than flaming wood, which produced less than 0.2 g kg^{-1} (McKenzie et al., 1995). Estimates of ethylene emissions from burning in agricultural and forestry activities in Canada have not been made, and are considered to be very small relative to other sources (National Research Council of Canada, 1985). Since fires are essentially point sources of ethylene, and since diffusion and dilution rapidly reduce ethylene levels as the distance from the fire increases (Gerakis et al., 1978), physiologically significant levels of ethylene are likely to occur only in areas near forest or agricultural fires (Abeles, 1982).

On an annual average basis (27-year average, from 1969 to 1995), approximately 85,000 ha of productive (capable of yielding 50 m^3 ha^{-1} of gross roundwood volume) and potentially productive (capable of producing a productive stand within 120 years) forests were burned per year. Volume of wood lost (coniferous plus smallwood deciduous) averaged 2,846,000 m^3 per year. yielding an average loss of 33 m^3 ha^{-1}. Average annual ethylene emissions from these fires is estimated using the following assumptions: average green weight of 600 kg m^{-3} for trees (pine, spruce, aspen), emissions of 1 g ethylene per kg of wood burned, and complete combustion. With these assumptions, 2,500 tonnes of ethylene per year are estimated to be emitted into the atmosphere from forest fires in Alberta. Until actual measurements of ethylene emissions from Alberta forest fires are made, this value can not be verified.

Jerman and Carpenter (1968) measured ethylene levels of up to 3% (by volume) in the smoke generated by municipal waste incineration. Up to 17,250 μg m^{-3} ethylene was detected in the flue gases of burned municipal waste in Babylon, NY, however, under good combustion conditions ethylene emissions were much lower (Carotti and Kaiser, 1972). The amount of ethylene generated depended upon the type of material burned, and the water content of the waste. Municipal waste incineration does not contribute significantly to atmospheric ethylene levels in Alberta.

Ethylene levels in ambient urban air are primarily the result of vehicular activity (Nassar and Goldbach, 1979). Gasoline itself does not contain ethylene (Stephens and Burleson, 1967). Darley et al. (1966) estimated that 0.4% of the gasoline burned in an engine was released as ethylene. This value has likely changed with the modernization of gasoline engines and emission controls, along with developments in gasoline additives and technologies. Ethylene emissions from vehicular sources are presented in Table II. Vehicular emissions contributed between 84 and 98% of the ethylene in urban air in the morning hours in downtown Los Angeles (Lonneman et al., 1974). Emissions from vehicles at cold start-up did not differ from roadway emissions (warm vehicles) (Doskey et al., 1992).

TABLE II
ETHYLENE EMISSIONS FROM VARIOUS ANTHROPOGENIC COMBUSTION SOURCES

Combustion Source	Ethylene Emissions	Reference
Residential wood combustion	1.13 kg tonne^{-1}	NRC (1995)[†]
Slash burning	0.15 kg tonne^{-1}	NRC (1995)
Wigwam burners	0.41 kg tonne^{-1}	NRC (1995)
Automobile (gasoline)	3.8 kg yr^{-1}	NRC (1995)
Light-duty trucks (gasoline)	4.4 kg yr^{-1}	NRC (1995)
Medium-duty trucks (gasoline)	9.3 kg yr^{-1}	NRC (1995)
Heavy-duty trucks (gasoline)	30.8 kg yr^{-1}	NRC (1995)
Agricultural equipment (gasoline)	1.9 kg$\bullet 10^{-3}$ l^{-1}	NRC (1995)
Heavy-duty construction equipment (gasoline)	3.3 kg$\bullet 10^{-3}$ l^{-1}	NRC (1995)
Industrial engines (gasoline)	3.2 kg$\bullet 10^{-3}$ l^{-1}	NRC (1995)
Railway locomotives (diesel)	1.2 kg$\bullet 10^{-3}$ l^{-1}	NRC (1995)
Heavy-duty trucks (diesel)	16.8 kg yr^{-1} veh^{-1}	NRC (1995)
Agricultural equipment (diesel)	0.8 kg$\bullet 10^{-3}$ l^{-1}	NRC (1995)
Construction vehicles (diesel)	0.4 kg$\bullet 10^{-3}$ l^{-1}	NRC (1995)
Other equipment (diesel)	0.5 kg$\bullet 10^{-3}$ l^{-1}	NRC (1995)

Light-duty vehicles (measured in 2 tunnels):
  Fort McHenry Tunnel (Baltimore MD)
  Tuscarora Mountain Tunnel (PA)
	
	43 mg veh-mile^{-1}
	27 mg veh-mile^{-1}
		Gertler et al. (1996)

Light-duty vehicles:
  Fort McHenry Tunnel (Baltimore MD)
  Tuscarora Mountain Tunnel (PA)
	
	35.3 mg veh-mile^{-1}
	23.2 mg veh-mile^{-1}
		Sagebiel et al. (1996);
		Zielinska et al. (1996)

Composite of vehicle types:
  Chicago IL Roadway
  Vehicle cold start
	
	6.98 (wt%) of total NMHC
	5.40 (wt%) of total NMHC
		Doskey et al. (1992)

Heavy-duty vehicles:
  Fort McHenry Tunnel (Baltimore MD)
  Tuscarora Mountain Tunnel (PA)
	
	50.8 mg veh-mile^{-1}
	34.9 mg veh-mile^{-1}
		Sagebiel et al. (1996);
		Zielinska et al. (1996)

Diesel motors (2 makes, 11 heavy duty diesel fuels)	31.5 mg km^{-1} to 102 mg km^{-1}	Sjögren et al. (1996)

[†]   NRC (1985) = National Research Council of Canada (1985)

[††] veh-mile = vehicle-mile

Recently, regulations requiring increased oxygen content of gasoline (increased from to 1.8 to 2.7% by weight) came into effect in several CO non-attainment areas of the United States. Increased oxygenation reduces CO and total VOC emissions; NO_x emissions remain constant. Total emission of ethylene decreased in proportion to the general reduction (18%) of VOC emissions as a result of increased oxygenation of gasoline (Kirchstetter et al., 1996). Ethylene comprised 7.8% of the VOC emissions (by weight) from gasoline containing 0.3% oxygen (MTBE was the only oxygenate), and 7.2% (by weight) of the emissions from high oxygenate fuel (2.0% by weight; oxygenates were 80% MTBE, 20% ethanol). Similar values of 8.1 to 11.2% (by weight) of ethylene in the total VOC mass emitted from light-duty vehicles were

Facility	Stack	Storage	Fugitive	Other	Total
Union Carbide Ethylene Glycol Plant, Prentiss	161.49	0.00	5.96	0.00	167.45
Dow Chemical Canada Inc., Fort Saskatchewan	43.00	0.01	100.00	7.10	150.11
Novacor Chemicals, Joffre	54.00	1.10	51.00	0.00	106.10
Syncrude Canada Ltd., Fort McMurray	50.45	0.00	0.21	0.00	50.66
Celanese Canada Ltd., Edmonton	25.00	0.00	2.50	0.38	27.88
AT Plastics Inc., Edmonton	77.56	17.52	103.00	0.00	198.08
Imperial Oil Strathcona Refinery, Edmonton	2.07	0.00	15.24	0.00	17.31
Petro-Canada Refinery, Edmonton	0.00	0.00	7.40	0.00	7.40
Shell Canada Products Ltd. Styrene Monomer Manufacturing Plant, Fort Saskatchewan	0.00	0.00	1.68	0.00	1.68
Totals	413.57	18.63	286.99	7.48	726.67

† Data from Environment Canada (1994)

reported by Gertler *et al*. (1996).

Other combustion processes (residential wood burning, office heating, tobacco smoking) produce ethylene. Those which have been quantified (emission factors) are presented in Table II.

3.2.2 Industrial Sources

Ethylene is used as a feedstock in a wide range of industrial processes leading to a diversity of end-products (Kniel *et al*., 1980), many of which are plastics. Therefore, petrochemical processing facilities which produce ethylene (by dehydrogenation of ethane), or use ethylene, are typical sources of anthropogenically-released ethylene.

At industrial facilities, ethylene may be released from stacks and flares, or as a result of leaks in pipe fittings (fugitive emissions). Environment Canada (1994) lists nine Alberta facilities which reported ethylene releases. These emissions are presented in Table III. Underground injections of ethylene are not included in Table III, since these injections do no directly contribute to atmospheric ethylene levels. A total of 726.67 tonnes was released into the air in Alberta in 1994 from these industrial sources, up from 561.86 tonnes in 1993 (Environment Canada, 1993). Stack and fugitive emissions were the largest sources of ethylene.

Flare emissions contain ethylene, and the amount of ethylene released depends upon the composition of the gas flowing to the flare (ethylene, methane, other hydrocarbons, condensate vapour, water, etc.), as well as the environmental conditions (especially wind) (Strosher, 1996). Flares at petrochemical facilities are designed to combust ethylene and other organic compounds

TABLE IV
SUMMARY OF ETHYLENE EMISSIONS FROM EXPERIMENTAL LABORATORY AND FIELD FLARES, AND FROM TWO OILFIELD BATTERY FLARES[†]

Experimental Flares Under Laboratory Conditions			
Flare Gas	Combustion Conditions	Ethylene Detected within Flame	Ethylene Detected outside Flame
Methane	Laminar Flow[‡]	1.25 g m^{-3}	—
Methane	Transitional[¶]	1.54 g m^{-3}	150 mg m^{-3}
Methane	Turbulent[§]	1.02 g m^{-3}	220 mg m^{-3}
Propane	Turbulent	1.56 g m^{-3}	180 mg m^{-3}
Natural Gas	Turbulent	1.10 g m^{-3}	160 mg m^{-3}
Methane + 15% Heptane			2.34 mg m^{-3}
Methane + 23% Heptane			1.64 mg m^{-3}
Methane + 32% Heptane			8.30 mg m^{-3}
Experimental Flares in Open Atmosphere with Calm Winds			
Flare Gas	Combustion Conditions	Ethylene Detected 25 to 50 cm away from Flame	
Natural Gas	Turbulent	0.1 to 0.5 mg m^{-3}	
Natural Gas + 15% Condensate Vapour	Turbulent	0.1 to 6.5 mg m^{-3}	
Natural Gas + 23% Condensate Vapour	Cross Winds	0.1 to 0.6 mg m^{-3}	
Operating Sweet and Sour Gas Battery Flares			
Flare Gas	Ethylene Detected		
	1 to 2 m from Flame	4 to 5 m from Flame	8 to 9 m from Flame
Sweet Solution Gas @ 1 to 2 m^3 min^{-1}	17 mg m^{-3}		
Sweet Solution Gas @ 5 to 6 m^3 min^{-1}		27 mg m^{-3}	9 mg m^{-3}
Sweet Solution Gas + liquid fuel + water	26 mg m^{-3}		
Sweet Solution Gas + liquid fuel	43 mg m^{-3}		
Sour Solution Gas	6 mg m^{-3}		

[†] Data from Strosher (1996).
[‡] Laminar flow conditions were considered to be optimal for combustion (no turbulence or cross winds).
[¶] Transitional flames contained significant flickering.
[§] Turbulent conditions caused highly variable flames.

in the event of facility upset. Ethylene emissions from these flares depend upon the extent of hydrocarbon combustion efficiency within the flare flame. Within the flames of solution gas flares, ethylene is produced as a product of pyrolytic reactions within the flame (Strosher, 1996). The majority of ethylene generated within the flame is combusted in the outer combustion zone.

Increased turbulence, or increased cross-winds, decreases combustion efficiency within the flame, and therefore, under these conditions, ethylene emissions increase. This report is particularly relevant to Alberta given there are approximately 5,300 flares in the province (Energy and Utilities Board, 1995, cited in Strosher, 1996). Emissions of ethylene from experimental laboratory and field flare systems, and operating sweet gas (no H_2S) and a sour gas (H_2S present) flares are presented in Table IV. The latter two flares were situated at battery sites, however, the sweet gas battery site was much larger than the sour gas site. Approximately 8,000 m^3 per day was sent to flare at the sweet gas site, while 650 m^3 were sent to flare at the sour gas site. Therefore, quantitative comparison of ethylene emissions from sweet and sour gas flares based on this work is not possible. This investigation represents the first time that VOC characterization and emissions from flares were determined, and hence, there is insufficient information to generalize to flare emissions province-wide.

Based on the emissions presented in Table IV, and on calculated emission rates for each of these two flares, plume dispersion modelling was used to predict maximum ground level ethylene levels which might occur as a result of incomplete combustion within the flares (Strosher, 1996). On a daily average basis, a maximum of 0.5 $\mu g\ m^{-3}$ is predicted to occur within 3 km of the sweet gas flare. This is in addition to any ethylene already present in the ambient air (e.g. as a result of ethylene production from vegetation). On an annual average basis, flaring at this site is predicted to increase ethylene concentrations by 0.01 $\mu g\ m^{-3}$. Increases of 0.02 $\mu g\ m^{-3}$ (daily average) and 0 $\mu g\ m^{-3}$ (annual average) are expected to occur within 3 km of the sour gas site. It is important to recognize that this is the first study of this type, and that these results are specific to the two sites investigated. Emissions from other flares will vary depending upon the composition of the gas being flared, the size of the flare, the environmental conditions at the time of flaring, and flare design.

3.2.3 Other Sources

Ethylene is released from activities in agriculture and forestry. These include emissions from stationary and field machinery, as presented in Table II. Additionally, ethylene release from crops as a result of application of chemical compounds (herbicides, growth regulators) also contributes to elevated ethylene levels on a site-specific basis. The agricultural compound ethephon (2-chloroethylphosphonic acid) is used to modify plant growth and development. Ethephon releases ethylene following incorporation into the plant. In Alberta, ethephon has been used to prevent lodging in cereal crops, the mode of action being primarily the reduction of stem elongation (Taylor *et al.*, 1991; Foster and Taylor, 1993). The ethylene diffuses out of the plant and into the atmosphere. Thus, applications of ethephon eventually contribute to atmospheric ethylene levels. At present, ethephon use in Alberta is limited.

4.0   ENVIRONMENTAL FATE AND BEHAVIOUR

Ethylene is naturally produced and metabolized by microorganisms, plants and animals. Additionally, ethylene is chemically reactive, and reactions which occur in ambient air remove ethylene from the atmosphere. Some of these reactions lead to the formation of ground-level ozone and photochemical smog.

4.1 Physical and Chemical Removal of Ethylene from Ambient Air

4.1.1 Chemical Removal of Ethylene

Ethylene is one of the more reactive VOCs and is oxidized in the atmosphere to form intermediate compounds (secondary pollutants), which will eventually break down to carbon dioxide and water. Estimates of the lifetime of ethylene in the troposphere have ranged from several hours (Bufalini *et al.*, 1976; Simpson, 1995) to just a few (<7) days (Darnall *et al.*, 1976, Howard, 1976). There are literally hundreds of chemical reactions and photochemical cycles associated with the destruction of ethylene in the troposphere. The chemical mechanisms involved are complex and their rates dependent on the actual physical conditions as well as the presence of a large variety of potentially available reactants and intermediates. Only a few major representative routes will be discussed.

Although ethylene can be oxidized by species such as O_3 or NO_3, it is the hydroxyl radical (OH) which is central to the chemistry of ethylene in the troposphere. These radical-chain reaction processes in the troposphere are photochemically driven. The OH radical is primarily produced by the photochemical decomposition of ozone (O_3) by sunlight (equation 1) followed by hydrogen abstraction from water (equation 2).

(1)
$$O_3 \xrightarrow[< 320 \text{ nm}]{\text{sunlight}} O_2 + O*$$
ozone   oxygen

(2)
$$O* + HO_2 \longrightarrow 2OH$$
hydroxyl radical
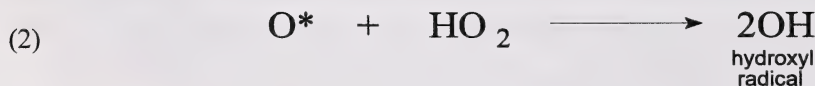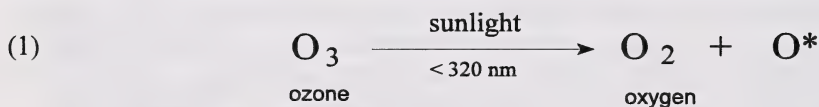
The resulting free OH radical is very reactive and can attack the double bond of the ethylene molecule (first step in equation 3). The reaction is fast with a rate constant of 8.52×10^{-12} cm^3 • molecule^{-1} • second^{-1} (Atkinson, 1994), and with the reaction rate being dependent on OH

concentration. For the average global OH concentration of 8.0×10^5 molecules • cm^{-3} (Prinn *et al.*, 1992) the half life of ethylene is about 27 hours. However, in more polluted urban areas where OH concentrations can reach 10^7 molecules • cm^{-3} (Eisele and Tanner, 1991) the half life is only about 2 hours. Through a series of subsequent chemical reactions ethylene can be transformed (equations 3 and 4) into other compounds (Finlayson-Pitts and Pitts, 1986).

(3) ethylene

(4)
decomposition (80%) → CH_2OH + formaldehyde

O_2 (20%) → HO_2 + glycolaldehyde
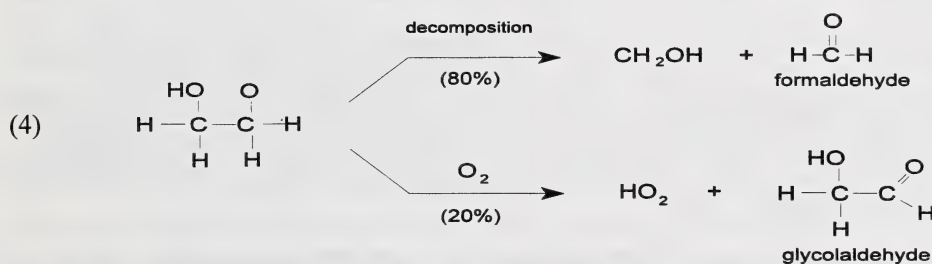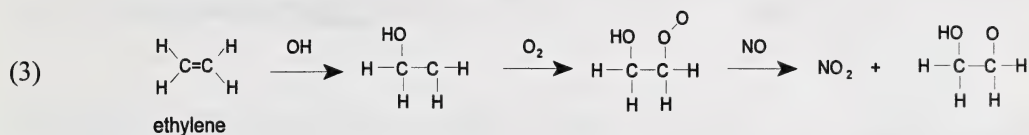
The organic products generated (in equation 4) can be further degraded through similar reactions to produce carbon dioxide and water. Several of the intermediates, especially the peroxides, may adversely affect vegetation (Hatakeyama *et al.*, 1995; Hewitt and Kok, 1991). More importantly, the process of ethylene oxidation will directly (equation 3) or indirectly (through HO_2 production in equation 4) generate NO_2, which can then lead to the formation of ozone (equations 5 and 6). Ozone is also phytotoxic (Bates, 1994).

(5)
$$NO_2 \xrightarrow[< 400\ nm]{sunlight} NO + O$$
nitrogen dioxide → nitric oxide

(6)
$$O + O_2 \longrightarrow O_3$$
oxygen → ozone
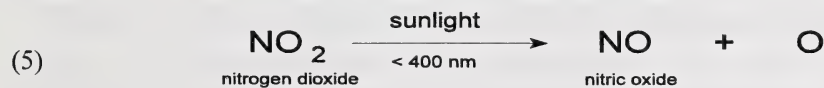
Ethylene has one of the highest photochemical ozone creation potentials of any hydrocarbon (Derwent *et al.*, 1996), and based on environmental chamber experiments can produce 2.6 moles of ozone per mole of ethylene (Carter, 1995). This ozone can go on to produce more OH radicals

(equations 1 and 2) or react directly with ethylene to form formaldehyde and the Criegee intermediate (equation 7), which both undergo further degradation (Niki *et al.*, 1983).

(7)
$$\underset{\text{ethylene}}{\overset{H}{\underset{H}{>}}C=C\overset{H}{\underset{H}{<}}} \xrightarrow{O_3} \left(\underset{\substack{H\ H \\ \text{Criegee} \\ \text{intermediate}}}{H-\overset{O}{\underset{H}{\underset{|}{C}}}-\overset{O}{\underset{H}{\underset{|}{C}}}-H} \right) \longrightarrow HCO_2 + \underset{\text{formaldehyde}}{H-\overset{O}{\overset{||}{C}}-H}$$
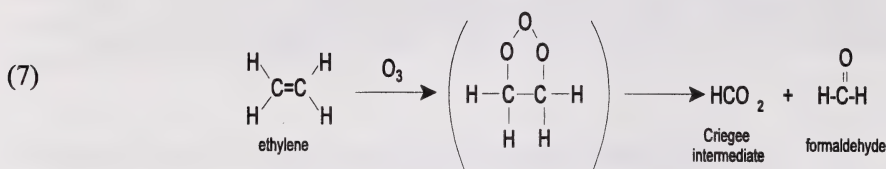
The rate of attack of ethylene by ozone is much slower than attack by the OH radical and is reflected in the substantially smaller ($k = 1.59 \times 10^{-18}$ cm^3 • molecule^{-1} • second^{-1}) rate constant (Atkinson, 1994).

Although oxidation by OH and ozone are the most important routes for ethylene removal in the daytime, oxidation by the nitrate radical (NO_3) dominates at night when there are no photochemical reactions (Wayne, 1991). The mechanism is thought to occur by nitrate addition across the double bond, which occurs slightly faster than attack by ozone. The rate constant ($k = 2.1 \times 10^{-16}$ cm^3 • molecule^{-1} • second^{-1}) is larger than for ozone attack, but much smaller than for the OH radical (Atkinson, 1992).

The photochemical oxidation of ethylene throughout the troposphere is a natural process and is the same as the chemistry of photochemical smog. Thus, the principles of ethylene degradation occurring in rural environments are not different from the principles of urban ethylene degradation (Bunce, 1994).

The complexity of both the large number of reactions and their interrelations has led to the extensive use of computer modelling to simulate conditions and species concentrations, as well as to evaluate reaction mechanisms (Simonaitis *et al.*, 1997; Carter, 1995). In urban environments where volume of automobile traffic dramatically increases the presence of NO_x and hydrocarbons (including ethylene), ethylene oxidation is faster than in rural settings. However, while ethylene is reduced at a greater rate in urban environments, the photochemical reactions involved contribute to elevated levels of secondary pollutants and smog. Since ethylene is short lived in the atmosphere, the emissions and chemistry associated with its removal is localized.

4.1.2 Physical Removal of Ethylene

Removal of ethylene in the atmosphere can occur via gas scavenging by atmospheric water (e.g. cloud, rain, fog) followed by precipitation to the Earth's surface. This wet deposition is proportional to the washout ratio (W_g) and varies with the Henry's Law constant (K_H) of ethylene:

$$W_g = [\text{ethylene}]_{\text{rain}}/[\text{ethylene}]_{\text{air}} = RT/K_H = RTC_w/P$$

where R is the ideal gas constant, T is the ambient temperature, P is the partial pressure and C_w is the aqueous solubility (Bidleman, 1988). This mechanism of wet deposition is an efficient

process for removing atmospheric gasses possessing a large W_g value (i.e. high aqueous solubility) and a long atmospheric lifetime (> 10 days). The W_g values for VOCs such as methane (0.035), ethane (0.050), or ethylene (0.128) are much lower than gasses like SO_2 (42.4), which can readily undergo vapour scavenging. These values were computed from gas solubilities (at 20°C) listed in Dean (1985). In addition, the chemical breakdown of ethylene is relatively fast giving an atmospheric lifetime of less than 7 days by most estimates. This combination of low aqueous solubility and short atmospheric lifetime make removal of ethylene by wet deposition of minor or negligible importance (Atkinson, 1995).

4.2   Biological Removal of Ethylene from Ambient Air

Soil bacteria and fungi both remove ethylene from the air spaces within the soil, with the amount removed dependent upon abiotic (temperature, soil moisture, oxygenation level) and biotic factors (number and types of species present). The ability of a soil to act as a sink varies among ecosystems, with agricultural soils (cropping, forage production) and forest soils differing in their ethylene-removal capabilities. Initial investigations suggested that the soil may act as sink for atmospheric ethylene (Abeles *et al.*, 1971). However, sorption by soils as a result of microbial activity was found to be minimal in a variety of soils (Smith *et al.*, 1973). The extent of ethylene removal from the atmosphere by the soil was investigated by Sawada *et al.* (1986) using a model which incorporates rates of diffusion into the soil and degradation within the soil. The model predicted that the soil would not act as a large sink for atmospheric ethylene, even in polluted atmospheres. Chemical reactions in the atmosphere were found to be 30 to 60 times more effective in removing ethylene from the air than was degradation within the soil. This investigation was conducted using the soil gathered from a *Cryptomeria japonica* forest; it is likely that soils from other ecosystems would behave differently. However, it is unlikely that ethylene removal by any soil would approach the chemical reaction and removal rates which occur in the atmosphere.

There is some evidence that ethylene is bound within soils as a result of non-biological processes. It is likely, however, that ethylene sorbed by soils in this fashion would either be re-released into the atmosphere, or eventually degraded by soil biota. As this is a slow process, degradation of ethylene by soil biota is unlikely to be a major ethylene removal process.

In order to act as a plant hormone, ethylene must be incorporated within the plant. Recognition of an ethylene signal may include metabolism of the ethylene, and its removal from air. Ethylene is metabolized by plants to ethylene oxide and ethylene glycol (Beyer, 1984; Dodds *et al.*, 1979), but the relative amounts removed by this process appear to be small.

5.0 MEASUREMENT AND MONITORING OF ETHYLENE

5.1 Collection of Samples

The proper choice of a sample container is important in obtaining an accurate measurement of ethylene concentration in air. Air samples are often collected in bags, syringes or other containers, and transported to a laboratory for analysis. Regardless of the container chosen, the system of sample collection and transport must be carefully checked to ensure that there is no ethylene loss (leakage, decomposition, adsorption to the container), or generation of ethylene as a result of chemical reactions within the container. If the sample containers are to be reused, it is equally important to ensure that the containers do not have an "ethylene memory" (release of ethylene adsorbed onto the inner lining into subsequently collected samples).

5.1.1 Sample Bags

Sample bags are available commercially, and have been used successfully (Sawada, 1985). Sample bags composed of aluminum foil sandwiched between polythene (inside) and polyester (outside), and of aluminum foil between polyester (inside and outside) have been successfully used to transport samples collected in the field to the laboratory (Rymen, 1979). However, the bags must be checked under the conditions in which they are to be used to ensure that they do not introduce artifacts into the sample. Either ethylene, or a contaminant chromatographically similar to ethylene, was found to be emitted from Teflon coating of sample containers used in aircraft sample collection systems (Rasmussen and Robinson, 1977; cited in Robinson, 1978). As a result, ethylene could not be quantified in these samples. Seila *et al.* (1976) found compounds with retention times similar to ethylene, propylene, acetylene, butene, 1-pentene, toluene, acetone and acetaldehyde as contaminants originating from Tedlar (polyvinylfluoride) bags exposed to light (wavelength of 310 to 390 nm). Irradiation also irreversibly altered the storage potential of these bags. If these bags are stored carefully (prevention of bag exposure to light), they can be used for ambient air storage prior to analysis.

Losses of 16% to 26% of organic compounds (toluene, trichloroethylene, and 1,2-dichloroethane) occurred during the first 24 hours of sample storage in commercial Tedlar bags (Wang *et al.*, 1996). Modification of the bags by replacing the hose valve with a septum reduced losses to 8% to 13% during the first 24 hours of sample storage. Losses from sample bags constructed by Wang *et al.* (1996) from bulk Tedlar film and Teflon valves was in the range of 4% to 11%. Wang *et al.* (1996) concluded that it was the hardware supplied with the sample bags, not the bag material itself, which was the cause of losses. Although ethylene losses from these bags was not investigated, leakage from the bags would not be chemical-specific. Thus, if sample bags are to be used for ethylene sampling, they must be tested prior to use to ensure that sample loss from the bag does not occur.

5.1.2 Syringes

Loss of ethylene from plastic and glass syringes has been quantified by Blankenship and

Hammett (1987). Ethylene losses approached 50% after 30 hours storage of a plastic syringe initially containing 11,500 $\mu g \ m^{-3}$ ethylene. Both diffusion out of the syringe and adsorption of ethylene to the syringe wall contributed to the loss. Loss from glass syringes was smaller, approaching 25% after storage of 11,500 $\mu g \ m^{-3}$ ethylene for 30 hours.

5.1.3 Glass and Metal Containers

Air samples were successfully collected and analyzed for ethylene (as well as a number of other non-methane hydrocarbons) in Sydney, Australia (Nelson and Quigley, 1982) using an active sampling system. Air was sucked through Teflon tubing into 400 ml glass pipettes, connected in series, and following a time sufficient to completely purge the system, the pipettes were sealed by closing attached Teflon valves. Pipettes were stored in the dark and transported to the laboratory for analysis. By sucking the air through the pipettes, rather than by pushing the air with the use of a pump, the need for a Teflon-coated pump was removed.

Evacuated stainless steel containers (2 litre) were used for sampling of air (Rudolph *et al.*, 1981). A rigorous cleaning and pretreatment regime was used to eliminate the possibility of cross-contamination of samples ("ethylene memory"). Samples were stored for as long as 3 months without detectable sample degradation. Brymer *et al.* (1996) determined that ethylene was not degraded, nor produced, within SUMMA polished canisters (stainless steel vessels treated to expose a smooth nickel and chromium oxide surface) during a 30-day sample storage period. The use of SUMMA containers for sampling of air for VOC analysis is now an established and accepted technique (Environmental Protection Agency, 1988), and these containers are currently being used in Alberta for VOC sample collection (Cheng *et al.*, 1997).

5.1.4 Mercuric Perchlorate

Air samples may be bubbled through a solution of mercuric perchlorate ($HgClO_4$), an ethylene trap (Abeles, 1973; Abeles *et al.*, 1992). In the laboratory, the trapped ethylene is released into the container headspace by addition of lithium chloride, and a subsample of the headspace is analyzed for ethylene. Absorption of ethylene into $HgClO_4$ minimizes ethylene losses during transport to the laboratory, however, $HgClO_4$ has the disadvantages of being corrosive, explosive and poisonous. Evidence of incomplete trapping, and incomplete release of ethylene from solution, has been presented (De Greef *et al.*, 1976). For these reasons, this method is seldom used.

5.2 Measurement of Ethylene

Chromatographic separation of ethylene from other compounds present in an air sample, followed by detection and quantification using a flame-ionization detector (FID) is the most common method of ethylene measurement. A diversity of chromatographic materials are available, and there is no one material which is preferred for ethylene purification and analysis. FID detectors have limitations, some of which may be overcome by modification of the chromatographic system, or by use of a different detector such as a mass selective detector, or a

Table V

**SELECTED ANALYTICAL METHODS WITH LOW DETECTION LIMITS FOR THE PURIFICATION
AND QUANTIFICATION OF ETHYLENE IN AIR**

Pretreatment	Purification System	Volume (ml)	Detector and Detection Limit ($\mu g\ m^{-3}$)	Reference
Concentration in a multisorbent (3 media) precolumn at -185°C and ambient temps.	DB-1 capillary column (60 m X 5 μm I.D.). Isothermal operation.	285	FID[¶] 0.22	Oliver *et al.* (1996)
Cryogenic trap (freeze-out tube) at -189°C.	GS-Alumina column (30 m X 0.53 mm I.D.). 4-stage temp. program.	400	FID 0.01	Goldstein *et al.* (1995)
Cryogenic trap (column of glass beads) at -189°C.	Stainless steel Durapak n-octane/Porasil C column (6 m X 3 mm O.D.)	200	FID 0.5	Colbeck and Harrison (1985)
Concentration in a multisorbent (2 media) precolumn at -35°C.	Spherosil X0B 075 packed column (7 m X 0.8 mm I.D.).	1,000	FID 0.008	Rudolph *et al.* (1981)
None	Porapak Q or Porapak N, packed column	5	FID 5.8	Nassar and Goldbach (1979)
Cryogenic trap (column of glass beads) at -189°C.	Durapak octane/Porasil C column (6.1 m x 1.5 mm O.D.). 3-stage temp. program.	400	MS 0.1[†]	Nelson and Quigley (1982)
Continuous flow-through system.	CO_2 laser tuned to ethylene (non-chromatographic system)	900 ml hr^{-1}	Photoaccoustic cell[‡] 0.007	Voesenek *et al.* (1990)
Continuous flow-through system.	CO_2 laser tuned to ethylene (non-chromatographic system)	900 ml hr^{-1}	Photoaccoustic cell 0.023	Harren *et al.* (1990)

¶   Abbreviations: FID, flame-ionization detector; MS, mass spectrographic detector.
†   Indicates the lowest ethylene concentration measured, not necessarily the detection limit.
‡   The CO_2 laser coupled with a photoaccoustic cell is not a chromatographic system, however these methods are presented here for comparison.

photo-ionization detector. The choice of detector will depend upon the concentrations to be analyzed. Some of the methods with low detection limits are presented in Table V; these are discussed in detail below.

5.2.1 Chromatographic Purification and Analysis of Ethylene

Several detectors for gas chromatographic quantitation of ethylene are available. The thermal conductivity detector (TCD) is particularly insensitive; ethylene can not be detected at the mg m^{-3} (e.g. 1,000 $\mu g\ m^{-3}$) level with this detector (Lamb *et al.*, 1973). The flame-ionization detector

(FID) is the most common detector used, having a lower detection limit of about 12 µg m^{-3} in a 5 ml sample (Abeles *et al.*, 1992). The amount of sample which can be directly injected onto a chromatograph is generally limited to 5 ml, as larger volumes will extinguish the detector flame. Because the concentration of ethylene in ambient air is generally low, analysis of large air samples may be necessary in order to obtain reliable results. Injection of larger volumes onto a precolumn which traps the ethylene but releases most of the other gases to atmosphere, overcomes many of the problems associated with measurement of low ethylene concentrations. The traps are made out of tubing (usually stainless steel) packed with molecular sieves (Harbourne *et al.*, 1973) or with chromatographic media, such as one of the Poropak materials (De Greef *et al.*, 1976; Galliard and Grey, 1969; Reid and Watson, 1981; Stephens and Burleson, 1969) or dimethyl sulfolane-coated supports (Stephens and Burleson, 1967). In either case, the sample is injected slowly onto the trap, which is kept cold (5°C for molecular sieve, -80°C for Poropak and dimethyl sulfolane materials), and is open to atmosphere on the downstream side of the media. The trap is then closed to atmosphere, heated, and opened to the analytical chromatographic column. The gas chromatograph carrier gas sweeps the ethylene into the analytical system. Using a precolumn (1 to 1.3 g of 13X molecular sieve in a 180 mm long section of ¼" I.D. stainless tubing) for preconcentration of ethylene lowered the detection limit to 2 µg m^{-3}, based on an injection of a 1 litre air sample (Harbourne *et al.*, 1973). Stephens and Burleson (1967), using a dimethyl sulfolane column and cold-trapping reduced the detection limit to 1 µg m^{-3} ethylene in 100 to 500 ml air samples. While cold-trapping is used primarily for preconcentration of ethylene from large gas samples, it also helps prepurify ethylene and remove compounds which interfere with the ethylene analysis (Galliard and Grey, 1969).

In some cases it may be necessary to remove moisture from the sample prior to injection onto the cold column; this can be accomplished by passing the sample through a potassium carbonate drying tube prior to injection onto the precolumn (Westberg *et al.*, 1974). Other water removal materials (silica gel, molecular sieve) removed the water but interfered with ethylene analysis.

An automated system has been developed for sampling and GC analysis of ozone precursor concentrations in ambient air (Oliver *et al.*, 1996). This system includes an automated sampler which collects air over a 57-minute period at 5 cm^3 min^{-1}, and passes this air through an organic vapour concentrator coupled with a cryo-focussing trap. This is a two-trap system, allowing the collection of a sample on one trap while the other is being purged. A total of 285 cm^3 are thus sampled. At the end of the 57-minute collection period, the trap is purged with dry helium to remove water (which interferes with the chromatography), and the trapped compounds are desorbed at 230°C and swept onto a GC column. For ethylene, cryo-cooling of the trap (-185°C) was found to be unnecessary, with effective trapping of ethylene occurring at ambient temperatures. This makes the system much more useful for field use. The ethylene detection limit using this system was found to be 0.22 µg m^{-3}. Analysis of a sample containing low concentrations of ethylene and acetylene (at or below 12 µg m^{-3}) was not possible, since the two compounds were not resolved thus rendering quantitation impossible. It is also important to note that the data generated by this system essentially represents a one-hour average ethylene concentration due to the sampling of air over a 57-minute period.

An automated system which allows *in-situ* (unattended) sampling and analysis, with an ethylene detection limit of about 0.01 µg m^{-3}, has been described by Goldstein *et al.* (1995). Components of this system include a cryo-cooled preconcentrator and a gas chromatograph

equipped with an FID. Ethylene recovery and elution from the cryo-cooled column were consistent and near 100%.

Use of Durapak n-octane/Porasil C as an analytical column packing, a sub-ambient temperature program, and a GC equipped with an FID, allowed detection of ethylene as low as 0.6 μg m^{-3} (Colbeck and Harrison, 1985). Trapping of C_2 to C_5 hydrocarbons from a 500 to 1000 ml sample on a 12 cm x 1/8 inch I.D. stainless steel precolumn containing 5 cm of porous silica and 5 cm Carbosieve B (column temperature of -35°C), followed by analysis on a 7 m x 0.8 mm I.D. packed column containing Spherosil X0B 075 packing, lowered the ethylene detection limit to 0.008 μg m^{-3} (Rudolph et al., 1981).

Photoionization detectors (PID) which utilize a lamp which emits light in the UV range (120 nm) are more sensitive to ethylene than are FIDs. Detection limits are in the region of 0.1 to 0.5 μg m^{-3} in a 1 ml sample. Generally, smaller samples may be analyzed (maximum injection volume is usually 1 ml), and cold trapping isn't required. Chromatographs equipped with a PID may be portable, facilitating field use. PID technology is advancing rapidly, and improved chromatographic systems using PID are now entering the market. While there is no published information regarding absolute detection limits for ethylene, it is recognized that these systems are more sensitive than FID, and are more amenable for use outside of the laboratory.

Measurement of ozone levels based on the reaction of ozone with ethylene is a common technique (e.g. Perkins et al., 1993), but the reverse is also possible. Measurement of ethylene by chemiluminescence was used by Mohan Rao et al. (1983). The limit of detection by direct injection of 10 ml was 115 μg m^{-3} ethylene, however, by adding a cold-trap precolumn to the GC system, the detection limit was reduced to the 1 to 10 μg m^{-3} range (actual limit not given).

Sexton and Westberg (1984) attempted to both measure ozone levels and sample for ethylene at the same site. The use of ethylene as a reactant in the chemiluminescent ozone monitor resulted in contamination of the air samples subsequently analyzed for ethylene. Similar contamination of air samples from co-located ozone monitors was also reported by Arnts and Meeks (1981), who emphasized the importance of proper location selection and methodology when investigating hydrocarbon content of ambient air.

5.2.2 Laser Detection and Remote Sensing Systems

Harren et al. (1990) used a CO_2 laser coupled to a photoaccoustic detector to measure low concentrations of ethylene in air. The reported detection limit of this system was 0.023 μg m^{-3}, allowing the detection and measurement of ethylene released from a single orchid flower. Voesenek et al. (1990) used this system to monitor ethylene release from a single waterlogged plant of $Rumex$ spp. (whole plant). The detection limits reported (0.007 and 0.023 μg m^{-3}) are low, and ethylene levels between 0.6 and 1.2 μg m^{-3} were accurately detected. While the laser photoaccoustic system is very sensitive to ethylene, it is very expensive and delicate, making it difficult to build and operate in the field for routine monitoring.

Menzies and Shumate (1976) used a bistatic laser system to monitor ethylene levels across a highway in the Pasadena CA area. Absorbance of several known wavelengths of CO_2 laser light across an atmospheric path provided the basis for ethylene quantification. The detection limit

was not given. This technique has not been used routinely, probably due to the expense and difficulty of use of the laser apparatus relative to gas chromatographic techniques.

Ethylene may be measured by remote sensing instruments, although the methods currently available (Fourier-transform infrared spectrometer; non-dispersive infrared analyzer) appear to have large errors associated with them (Stephens *et al.*, 1996).

5.3 Quality Assurance and Quality Control (QA/QC) Protocols

In any survey of ethylene levels in ambient air, a Quality Assurance/Quality Control protocol is required. The QA/QC protocol, and subsequent validation of the data, for the Southern Oxidants Study 1992 Atlanta Intensive monitoring program provides a good review of the need for QA/QC, as well as a protocol for a QA/QC program (Apel *et al.*, 1995; Bernardo-Bricker *et al.*, 1995). Several laboratories were involved in the analysis of ambient air samples. In addition to the experimental samples, each laboratory was supplied with a series of standards which were analyzed each day to ensure correct instrument calibration and to verify retention time windows for identification of the target compounds (one of which was ethylene). A QA/QC protocol must be implemented for programs which use more than one instrument or facility for the measurement of ethylene in ambient air. In programs in which a single instrument will be used, proper calibration is required at regular intervals (daily at a minimum).

5.4 Monitoring Ethylene Plume Dispersal

Fugitive emissions from petrochemical facilities are a major anthropogenic source of ethylene (Table III). Measurement of such emissions is difficult, due to the diversity and number of individual sources. Monitoring of ambient ethylene around such facilities gives an indication of the total release of ethylene, including that portion due to fugitive emission. Monitoring and modelling of these fugitive emissions may be accomplished through the use of tracer gases. SF_6 and $CBrF_3$ were released near fittings suspected of releasing ethylene in amounts proportional to the suspected leakage of ethylene, and were monitored downwind of the facility (Siversten, 1983). Application of Gaussian models to the SF_6 data accurately predicted the ethylene concentration downwind of the facilities (Siversten, 1983).

5.5 Acetylene as a Marker of Ethylene Emissions from Automobiles

Atmospheric acetylene (C_2H_2) is almost exclusively produced by vehicular activity, and acetylene was thought to be resistant to photochemical degradation (Stephens and Burleson, 1967, 1969). Therefore, acetylene has been used as a marker of automobile emissions (Stephens and Burleson, 1967, 1969). In unreacted ambient air in Riverside CA, the ratio of ethylene to acetylene was found to be 0.81, similar to that found in other urban areas (Stephens and Burleson, 1969). However, Kopczynski *et al.* (1975) found that atmospheric acetylene levels may be reduced by unknown, but very effective, removal processes. Use of acetylene as a marker of automobile emissions was therefore suspect. Whitby and Altwicker (1978) suggest that ambient air acetylene levels and ratios with other hydrocarbons do provide useful and generally

accurate tools in air pollution studies. Greater knowledge of industrial and natural acetylene emissions and environmental reactions is required before the use of ethylene to acetylene ratios can be used as a quantitative tool in the estimation of automotive emissions (Whitby and Altwicker, 1978).

6.0 AMBIENT LEVELS

6.1 Remote and Rural Environments

Ethylene concentrations measured in rural and remote environments are summarized in Table VI. Levels in these locations are generally below 15 μg m^{-3}; these levels are considered to represent "background" ethylene levels.

Measurements of ethylene levels at Point Barrow, Alaska were attempted by Cavanagh *et al.* (1969). Ethylene did not completely separate from ethane in their chromatographic system, nor did they calibrate the instrument using standard ethylene (other compounds were used to calculate FID response). The concentration of the composite ethylene-ethane component did not exceed 0.09 μg m^{-3}. The only conclusion possible from this work is the qualitative statement that background ethylene levels in Alaska are expected to be quite low.

Ethylene concentrations in air in and above the boundary layer in both northern and southern latitudes were relatively constant, averaging approximately 0.2 μg m^{-3} (Rasmussen and Khalil, 1982). Levels between 0.6 and 1.3 μg m^{-3} were measured in samples collected above Japan from between 300 and 2,000 m above sea level (Sawada, 1985). Analysis of wind patterns and velocity suggested that anthropogenic sources did not contribute to these levels.

Measurements of ethylene levels in a subalpine coniferous forest northwest of the City of Calgary showed a cyclical pattern of ethylene levels, with the highest concentrations occurring at 1300 hr (14 μg m^{-3}) and the lowest at 2100 hr (3 μg m^{-3}) (Reid and Watson, 1981). This cycle was attributed to ethylene produced by vegetation during the daylight hours. The measurements by Reid and Watson (1981) indicate that a summertime (late June) background level of ethylene in Alberta is in the range of 2 to 14 μg m^{-3}.

Emissions from soft and hard wood tree species in both dry and swamp environments in Louisiana generated ambient ethylene levels between 0.4 and 0.5 μg m^{-3} (Khalil and Rasmussen, 1992). These levels are an order of magnitude lower than levels observed in Alberta forest environments (Reid and Watson, 1981).

6.2 Urban Environments

Ethylene concentrations in urban and suburban environments are summarized in Table VII. Observed levels vary from 4 μg m^{-3} in downtown Tulsa OK (Arnts and Meeks, 1981) to a high of 805 μg m^{-3} found in downtown Washington DC (Abeles and Heggestad, 1973). Since automobile exhaust contains high levels (282,900 μg m^{-3}) of ethylene (Neligan *et al.*, 1961), automobiles are the major sources of urban ethylene.

Concentrations between 40 and 69 μg m^{-3} were found in the eastern industrial areas of Calgary, and further to the east of this development (Reid and Watson, 1981). Ethylene concentrations decreased as distance from the city increased. Within the city, a maximum of 113 μg m^{-3} was reported during a winter temperature inversion. These inversions are known for trapping pollution at or near ground level, and for preventing wind at ground level. Levels between 14 to 69 μg m^{-3} were generally found in the city or downwind of the downtown core.

TABLE VI
ETHYLENE LEVELS IN AMBIENT AIR IN RURAL AND REMOTE LOCATIONS

Location, Date, Time of Day	Ethylene ($\mu g\ m^{-3}$)	Reference
Above and below boundary layer in both N. and S. latitudes. Jun. 1978	0.2	Rasmussen and Khalil (1982)
Boundary layers from 300 to 1200 m above sea level, Japan	0.6 to 1.3	Sawada (1985)
Subalpine coniferous forest, NW of Calgary AB, Aug. to Sept. 1981	3 to 14	Reid and Watson (1981)
Rural MO, Dec. 1972, 0800 to 0900 hr	4	Kopczynski *et al.* (1975)
Rural FL, 1000 to 1900 hr, May 18, 1976	2 to 4	Lonneman *et al.* (1978)
Rural OK, Jul. 27, 1978	<1	Arnts and Meeks (1981)
Rural ME, CA, WI, TX, IL, Summer 1975 to 1978	2 (max)	Sexton and Westberg (1984)
Elkton MO, 1975	4 (max)	Robinson (1978)
Louisiana, Dry and Swamp Forests, June 1990	0.4 to 0.5	Khalil and Rasmussen (1992)
50 km upwind of Mexico city (Pyramid of the Moon) 1230 hr, Feb. 21, 1993	0.7	Blake and Rowland (1995)
Rural NW England, Feb. to Mar. 1978	<14	Harrison and Holman (1980)
Rural NW England, summer 1983	2	Colbeck and Harrison (1985)

Pallas, Finland (high elevation)
  Jan. 1993/4
  Jul. 1993/4
Uto, Finland (Baltic Sea island)
  Dec. 1993/4
  Jun. 1993/4
	
	0.6
	0.05
	
	1.0
	0.1
		Laurila and Hakola (1996)

Japan, fall 1980/1
  300 to 1200 m above sea level
  Fagus crenata forest
	
	0.6 to 1.3
	3 to 15
		Sawada (1985)

The median ethylene concentration in downtown Edmonton, AB during the period of December 1991 through November 1993 was 4.99 $\mu g\ m^{-3}$, based on samples collected over a 24-hour period, every sixth day (Cheng, *et al.*, 1997). In the eastern industrial area of Edmonton, the median ethylene level was 4.53 $\mu g\ m^{-3}$ (same sample collection protocol). These low levels of ethylene suggest that on a 24-hour average basis, ethylene levels in the urban airmass are typically low. This may be due to ethylene-ozone reactions. These data do not provide an indication of the maximum ethylene levels which occurred during the day, since samples collected over an entire day were analyzed.

Colbeck and Harrison (1985) compared ambient air hydrocarbon concentrations in samples taken from urban and "polluted" rural (downwind of urban centres) locations. Rural air samples (considered to represent background levels) contained an average of 2 $\mu g\ m^{-3}$ ethylene, while samples from urban locations averaged 49 $\mu g\ m^{-3}$. Polluted rural air samples contained 26 $\mu g\ m^{-3}$, indicating some dilution and degradation during transport from urban to rural locations.

Average annual ethylene levels in the Sarnia ON industrial area varied between 6 and 14 μg

TABLE VII
Ethylene Levels in Ambient Air in Urban and Suburban Environments

Location, Date, Time of Day	Ethylene ($\mu g\ m^{-3}$)	Reference

Calgary AB
  Roadside 1981
  U. of Calgary, Feb. to May 1981
  U. of Calgary, Jan. 27 1981(temperature
    inversion)
  Eastern (downwind) side, Feb. and May 1981
	
	12 to 24
	14 to 33
	113
	
	40 to 69
		Reid and Watson (1981)

Edmonton AB, Dec. 1991 to Nov. 1993
  Downtown
  East-side Industrial Area
	
	4.99
	4.53
		Cheng *et al.* (1997)

Sarnia ON, 1978 to 1983, average annual	6 to 14	Lambdon Industrial Society (1983)

California
  Los Angeles, 0700 to 0800 hr, fall 1967
  Los Angeles, 1200 to 1300 hr, fall 1967
  Azusa, 0700 to 1300 hr, fall 1967
  Azusa, 0500 to 1600 hr, fall 1967
  Riverside, 0815 hr, Jan. 23, 1968
  Pasadena CA, Freeway 1000 to 1200 hr
  Pasadena CA, Freeway 1600 hr
	
	89
	29
	21 to 24
	9 to 21
	144
	9
	39
		
		Altshuller *et al.* (1971)
		Altshuller *et al.* (1971)
		Altshuller *et al.* (1971)
		Gordon *et al.* (1968)
		Stephens and Burleson (1969)
		Menzies and Shumate (1976)
		Menzies and Shumate (1976)

St. Louis MO, 0800 to 0900 hr, Dec. 1972	39	Kopczynski *et al.*, 1975
Downtown Miami FL, 0800 hr, May 18, 1976	12	Lonneman *et al.*, 1978
Tulsa OK, Downtown 0953 to 1053 hr, Jul. 27, 1978 Tulsa OK, Suburban 0825 to 0925 hr, Jul. 27, 1978	4 5 to 7	Arnts and Meeks (1981)
Washington DC Downtown, summer day 1972 Washington DC Suburban, summer day 1972	805 45	Abeles and Heggestad (1973)
Metropolitan Denver CO, 0800 to 1200, Oct. 1971 to Feb. 1972	207 (max)	Hanan (1973)
Philadelphia PA, Suburban	6 to 117	Giannovario *et al.* (1976)

Mexico City, Mexico
  Downtown (Zocalo), 0600 hr, Feb. 21, 1993
  Downtown (Zocalo), 1200 hr, Feb. 18, 1993
  Tlalpan Highway, 1645 hr, Feb. 20. 1993
	
	18
	32
	193
		Blake and Rowland (1995)

Sydney, Australia, morning Sept. 1979 to Jun. 1980	14	Nelson and Quigley (1982)

Hamburg, Germany, 0900 to 1100 and
  1600 to 1900, summer 1976, high traffic area
Hamburg, Germany, 0900 to 1100 and
  1600 to 1900, summer 1976, low traffic area
Hamburg, Germany, night, summer 1976
Minden, Germany, late night, summer 1976
	173 (max)
	
	58 (max)
	
	12 to 23
	6
		Nassar and Goldbach (1979)

Delft, The Netherlands	18	Bos *et al.* (1977)
Urban Swansea, South Wales (early 1970's) Semi-rural Swansea, South Wales (early 1970's)	322 230	Harbourne *et al.* (1973)
Urban NW England, summer 1983 "Polluted" Rural England, summer 1983	49 26	Colbeck and Harrison (1985)
NW England, populated areas, Feb. to Mar. 1978	<9	Harrison and Holman (1980)

m^{-3} between 1978 and 1983 (Lambdon Industrial Society, 1983).

Ethylene levels in a suburban area of Philadelphia near several industrial facilities ranged from 6 to 117 µg m^{-3} (Giannovario *et al.*, 1976). The actual location, time of sampling (day, month, year) and sampling protocol were not described.

Ethylene concentrations of up to 805 µg m^{-3} have been detected in downtown Washington DC (Abeles and Heggestad, 1973). This is the highest ambient ethylene concentration reported in the literature. Levels diminished as the distance from the downtown core increased, reaching 45 µg m^{-3} outside the circumferential highway

Measurements of ethylene in the air near Swansea, South Wales indicated an average of 322 µg m^{-3} ethylene, with 230 µg m^{-3} in air samples taken on hillsides away from main roads and houses (Harbourne *et al.*, 1973). These are relatively high concentrations, and were attributed to heavy industrial and transportation activities.

In urban environments, peak ethylene levels generally correspond with peak traffic activity. In Hamburg, Germany, maximum concentrations of ethylene (173 µg m^{-3}) were observed near a city street during rush-hour (Nassar and Goldbach, 1979). Peaks were observed during both the morning (0900 to 1100 hr) and afternoon (1600 to 1900 hr) high-traffic periods. Levels at night fell to 12 to 23 µg m^{-3}, which for Hamburg, are close to background concentrations. A similar pattern was observed near a service station, away from heavy traffic, although overall levels were lower, peaking at about 58 µg m^{-3}. Ethylene levels over a Pasadena CA highway increased within minutes of increased traffic flow, as measured using a bistatic laser system (Menzies and Shumate, 1976). Because only 20% of the laser path length was over the highway, ethylene concentrations at the edge of the road (9 to 39 µg m^{-3}) were underestimated in this study. Vegetation in the vicinity of larger roads may be expected to respond to regular ethylene exposures resulting from vehicular activity.

Near an industrial area of Hamburg, combined rural and residential emissions resulted in 23 µg m^{-3} ethylene, with an additional 23 µg m^{-3} coming from urban and industrial areas. It was hypothesized that some of the urban/industrial ethylene reacted photochemically prior to measurement; this was substantiated with the measurement of lower ethylene concentrations during the summer when solar radiation was at its highest (Nassar and Goldbach, 1979).

Ethylene levels of 18 µg m^{-3} were observed in Delft, The Netherlands (Bos *et al.*, 1977). Half of this amount was attributed to industrial sources, with the other half arising from automobiles.

6.3   Industrial Environments

Some industrial processes generate and emit ethylene into the air. The literature describing ambient ethylene levels in and around industrial areas is summarized in Table VIII.

Plume chemistry analyses of the emissions from the Syncrude and Suncor oil sands facilities in the Fort McMurray, Alberta, area were conducted in the winter, spring and summer of 1980 (Bottenheim, 1984). Ethylene concentrations within the Syncrude plume ranged from 0.3 to 16 µg m^{-3}, with higher concentrations found nearer the source stack. The highest values tended to occur during the summer months.

TABLE VIII
ETHYLENE LEVELS IN AMBIENT AIR IN INDUSTRIAL ENVIRONMENTS

Location, Date, Time of Day	Ethylene ($\mu g\ m^{-3}$)	Reference
Fort McMurray AB, 1980	16 (max)	Bottenheim (1984)
Industrial area near San Francisco CA, Sept. 1975	3.5 (max)	Sexton and Westberg (1979)
Trombay, Bombay, India, Dec. 1981 Trombay, Bombay, India, Jan. 1982	2 to 38 5 to 137	Mohan Rao *et al.* (1983)
Trombay, Bombay, India, Monthly for 1100 to 1300 hr and 1430 to 1630 hr, 1982	2 to 44 (mean) 138 (max)	Netravalkar and Mohan Rao (1984)
NW England, Feb. to Mar. 1978 Oil refinery Fertilizer manufacturing facility Near 1,1,1-trichloroethane, vinyl chloride monomer and perchloroethene manufacturing facility	<6 <1 <1 to 610	Harrison and Holman (1980)

Combined emissions from industrial facilities (petroleum refineries, power plants, chemical processing facilities and other industries) in the San Pablo Bay - Carquinez Strait - Suisun Bay channel (near San Francisco CA) increased ethylene levels from below the limit of detection (0.5 $\mu g\ m^{-3}$) to up to 3.5 $\mu g\ m^{-3}$ (Sexton and Westberg, 1979). Levels progressively increased as the number of sources contributing to the overall pollution burden increased.

Ethylene levels in Trombay, Bombay, India ranged from 2 to 38 $\mu g\ m^{-3}$ in December 1981, and from 5 to 137 $\mu g\ m^{-3}$ in January 1982 (Mohan Rao *et al.*, 1983). Trombay is located approximately 20 km from the city of Bombay, and is near two oil refinery sites. Most of the measurements indicated that only background levels of ethylene were present in the Trombay area. The source(s) which resulted in elevated ethylene levels was (were) not determined. Mean monthly ethylene concentrations for the periods of 1100 to 1300 hr and 1430 to 1630 hr ranged from 2 to 44 $\mu g\ m^{-3}$ ethylene (Netravalkar and Mohan Rao, 1984). Individual daily measurements showed a maximum of 138 $\mu g\ m^{-3}$. The highest levels were recorded in February 1992, and the lowest in July 1992.

Ethylene levels downwind of a refinery (<6 $\mu g\ m^{-3}$), a fertilizer manufacturing facility (<1 $\mu g\ m^{-3}$), and in some small (pop. 4,500 to 8,600) towns and a small (pop. 64,000) city (<9 $\mu g\ m^{-3}$) were not above levels found in rural areas (14 $\mu g\ m^{-3}$) (Harrison and Holman, 1980). However, levels around a facility manufacturing 1,1,1-trichloroethane, vinyl chloride monomer, and perchloroethene varied between <1 $\mu g\ m^{-3}$ to 610 $\mu g\ m^{-3}$, with the highest concentrations occurring at the point of impingement of the plume from the three facility stacks.

6.4   Other Environments

Gases produced from covered, vented landfills may contain ethylene. The amount of ethylene generated and released varies with the types of material in the landfill, the age of the landfill, and

the design and methods used to build and seal the site. The gas in venting pipes in the Gin Drinkers Bay landfill, Hong Kong, included an average of 2,300 µg m^{-3} ethylene, however, the pipes varied greatly in ethylene content (Wong and Yu, 1989a). Ethylene also escaped through the surface of the covering soil, since a gas preventing blanket was not used to seal the landfill (Wong and Yu, 1989b). In neither of these studies (Wong and Yu, 1989a, b) was total ethylene emission from the landfill calculated.

Soil gas concentrations over and near landfill sites in Florida were measured by Bausher (1991). Levels as high as 85,100 µg m^{-3} ethylene were observed in gas sampling tubes in the immediate area of the landfills, with levels in the soil diminishing as the distance from the landfill increased. No ambient air ethylene concentrations were reported. Valencia orange trees showed signs characteristic of ethylene exposure (wilting, leaf abscission), however, since other gases (oxygen, carbon dioxide, methane) also varied with the distance from the landfill, separating the effects and attributing some or all of them to ethylene is not possible.

7.0 ENVIRONMENTAL EFFECTS OF ETHYLENE

While there have been many research projects devoted to determining the role of ethylene in plant growth and development, and to determining the effect of applied ethylene on plants, most studies presented in the literature contain data resulting from exposures of plants to concentrations well in excess of those expected to occur in ambient air. The following review emphasizes the results from studies in which low levels of ethylene were used (less than 1,150 μg m^{-3}), although results of experiments in which higher levels were used are presented for comparison. Levels above 1,150 μg m^{-3} will have environmental effects, and therefore will not be used in establishing an Alberta ethylene guideline.

7.1 Microorganisms

No information regarding the effect(s) of ethylene at ambient levels (less than 1,150 μg m^{-3}) was found. Some evidence of the fungistatic effects of ethylene was reviewed by the National Research Council of Canada (1985), with the conclusion that the evidence for ethylene fungistasis is weak. Ethylene does have an effect on the nodulation of legume roots by root nodulating bacteria, and may affect the interaction of plant roots with other soil microorganisms. These data are discussed in *Section 8.2.4, Plant Growth*.

7.2 Plants

7.2.1 Germination

Increased seed germination in some species has been observed in response to ethylene, while in other species ethylene either retards germination or has no effect (Table IX). Injections of ethylene (1,150 μg m^{-3} and above) into the soil in pots containing seeds of redroot pigweed (*Amaranthus retroflexus* L.) and large and small seeds of common cocklebur (*Xanthium pensylvanicum* Wallr.) increased total germination (Egley, 1980). Ethylene injections of 1,150 μg m^{-3} and above promoted germination in several other species, and did not affect many others (Taylorson, 1979). These experiments were conducted to investigate the potential for stimulating weed germination, rather than to determine the lowest concentration of ethylene required to have an effect. Germination of redgrass (*Themeda triandra*), an African fire-climax grass, was not affected by ethylene in the concentration range of 1 to 1,150,000 μg m^{-3} (in 10-fold increments) or by application of ethephon in a similar range of concentrations (Baxter *et al.*, 1994). Lettuce seed germination was promoted by exposure to smoke, however, exposure to ethylene did not stimulate germination to the same degree (Jäger et al., 1996). Thus, ethylene component of smoke (from burning vegetation) is not responsible for the stimulation of germination in response to smoke exposure.

7.2.2 Photosynthesis

Ethylene may affect photosynthesis by one or more mechanisms. The effect may be on the

TABLE IX
EFFECTS OF ETHYLENE ON GERMINATION

Species	Ethylene ($\mu g \ m^{-3}$)	Effect	Reference
Redroot Pigweed (*Amaranthus retroflexus*)	>1,150 (light and dark)	Promotive	Egley (1980) Taylorson (1979)
Tumble Pigweed (*Amaranthus spinosus*)	>1,150 (light and dark)	Promotive	Taylorson (1979)
Cocklebur (*Xanthanum pensylvanicum*)	>1,150 (light and dark)	Promotive	Egley (1980)
Ragweed (*Ambrosia artemisiifolia*)	>1,150 (light and dark)	Promotive	Taylorson (1979)
Lambsquarters (*Chenopodium album*)	>1,150 (light and dark)	Promotive	Taylorson (1979)
Purslane (*Portulaca oleracea*)	>1,150 (light)	Promotive	Taylorson (1979)
Red sorrel (*Rumex acetosella*)	>1,150 (light)	Promotive	Taylorson (1979)
Curly dock (*Rumex crispus*)	>1,150 (light)	Promotive	Taylorson (1979)
Broadleaf dock (*Rumex obtusifolius*)	>1,150 (light)	Promotive	Taylorson (1979)
Rough cinquefoil (*Potentilla norvegica*)	>1,150 (light and dark)	Inhibitory	Taylorson (1979)
Horsenettle (*Solanum carolinense*)	>1,150 (light and dark)	Inhibitory	Taylorson (1979)
Redgrass (*Themeda triandra*)	1.15 to 1,150,000	None	Baxter *et al.* (1994)
Lettuce (*Latuca sativa* cv. Grand Rapids)	1,150 to 2,300 5,750 to 115,000	None Promotive	Jäger *et al.* (1996)
10 grass species	>1,150 (light and dark)	None	Taylorson (1979)
21 broadleaf species	>1,150 (light and dark)	None	Taylorson (1979)

CO_2 uptake (Pallas and Kays, 1982; Squier *et al.*, 1985). Ethylene may affect carbon assimilation by inhibiting RuBP-carboxylase activity (the enzyme which fixes CO_2 within the plant cell) (Squier *et al.*, 1985). Electron transport in the light reactions (the conversion of light energy into chemical energy in the plant cell) may be reduced, therefore, the plant may have less chemical energy to devote to CO_2 fixation (Wullschleger *et al.* 1992). Distribution of fixed carbon may be altered in plants exposed to ethylene; redistribution of photosynthate within plants has been observed following treatment with ethephon, an ethylene-releasing compound (Woodrow *et al.*, 1988). Each of these effects has been demonstrated to occur in one or more species, however, given the physiological complexity of photosynthesis and photosynthate partitioning, there has been insufficient research to determine if the observed effects are general across the plant kingdom, or represent species-specific responses to ethylene exposure.

The literature describing the effects of ethylene on photosynthesis is summarized in Table X. As described in *Section 4.2, Anthropogenic Production of Ethylene*, vehicular exhaust is the major man-made source of ethylene. The highest levels of ethylene in urban centres occur in the morning and late afternoon, coincident with periods of active photosynthesis.

Reductions in photosynthesis in soybean (*Glycine max* L.) in response to ethylene treatment occurred slowly, but became progressively larger as the fumigation period increased (Squier *et al.*, 1985). By the end of the 28-hour fumigation period, photosynthesis in the control plants had increased by 20%, while photosynthesis in plants exposed to 112 and 281 $\mu g \ m^{-3}$ ethylene remained constant during this period. Thus, relative to control, exposure to 112 and 281 $\mu g \ m^{-3}$

TABLE X
EFFECTS OF ETHYLENE ON PHOTOSYNTHESIS

Species	Ethylene (μg m^{-3})	Exposure Duration	Effect	Reference
Soybean (*Glycine max*)	112	28 hours	20% Decrease	Squier *et al.* (1985)
	281	28 hours	20% Decrease	Squier *et al.* (1985)
	589	28 hours	50% Decrease	Squier *et al.* (1985)
Peanut (*Arachis hypogaea*)	115	2 hours	No effect	Kays and Pallas (1980)
	112	28 hours	8 to 12% Decrease	Squier *et al.* (1985)
	288	2 hours	33% Decrease	Kays and Pallas (1980)
	1,150	2.5 hours	10 to 35% Decrease	Pallas and Kays (1982)
	281 to 589	28 hours	40 to 50% Decrease	Squier *et al.* (1985)
	1,150	6 hours	68% Decrease	Pallas and Kays (1982)
Tobacco (*Nicotiana tobaccum*)	589	28 hours	40% Decrease	Squier *et al.* (1985)
	1,150	28 hours	>80% Decrease	Squier *et al.* (1985)
	2,300	28 hours	>80% Decrease	Squier *et al.* (1985)
Green ash (*Fraxus pensylvanica*)	281	28 hours	10% Decrease	Squier *et al.* (1985)
	589	28 hours	10% Decrease	Squier *et al.* (1985)
Potato (*Solanum tuberosum*)	575	3 hours	10% Decrease	Govindarajan and
	1,150	3 hours	18% Decrease	Poovaiah (1982)
	1,150	2.5 hours	No effect	Pallas and Kays (1982)
Jerusalem artichoke (*Helianthus tuberosus*)	1,150	2.5 hours	7% Decrease	Pallas and Kays (1982)
Sunflower (*Helianthus annuus*)	1,150	2.5 hours	12% Decrease	Pallas and Kays (1982)
Sweet potato (*Ipomoea batatas*)	1,150	2.5 hours	10% Decrease	Pallas and Kays (1982)
Corn (*Zea mays*)	≤4,600	28 hours	No effect	Squier *et al.* (1985)
Green bean (*Phaseolus vulgaris*)	1,150	2.5 hours	No effect	Pallas and Kays (1982)
Pea (*Pisum sativum*)	1,150	2.5 hours	No effect	Pallas and Kays (1982)
Sensitive plant (*Mimosa pudica*)	1,150	2.5 hours	No effect	Pallas and Kays (1982)
White clover (*Trifolium repens*)	1,150	2.5 hours	No effect	Pallas and Kays (1982)

ethylene resulted in a statistically significant reduction in photosynthesis following a 28-hour ethylene treatment. Plants exposed to 589 μg m^{-3} ethylene exhibited a 50% reduction in photosynthesis relative to the initial rate, well below the rate in control plants at the end of the experiment.

Photosynthesis in peanut (*Arachis hypogaea* L.) rapidly decreased after the initiation of fumigation with 281 and 589 μg m^{-3} (Squier *et al.*, 1985). Photosynthesis in peanut plants exposed to 112 μg m^{-3} remained relatively constant, while an 8 to 12% increase was observed in control plants. By the end of the 28-hour treatment period, plants treated with 112 μg m^{-3} had recovered to the control photosynthetic rate, while the rate in plants exposed to 281 and 589 μg m^{-3} remained 40 to 50% below that in the controls. Inhibition (33% reduction) of photosynthesis in peanut was observed by Kays and Pallas (1980) following treatment of 3-week old peanut leaves to 288 μg m^{-3} ethylene for 2 hours. A response was not observed at 115 μg m^{-3}, and was saturated at 1,150 μg m^{-3}. Photosynthetic inhibition was increased by longer ethylene exposures.

Photosynthesis returned to normal in all plants treated for short periods of time (0.5 to 2 hours). A constant amount of inhibition (18%) was observed at several light intensities; thus the effect is not expected to differ under brighter or cloudier conditions. Photosynthesis in peanut leaves was inhibited by increasing duration of exposure to 1,150 $\mu g\ m^{-3}$ ethylene (Pallas and Kays, 1982). Inhibition occurred rapidly after addition of ethylene. Photosynthesis was reduced by as much as 68% after a 6-hour exposure to 1,150 $\mu g\ m^{-3}$. Photosynthesis in leaves exposed for less than 6 hours had fully recovered by the following day, however, in the 6-hour treatment, recovery required an additional day. Decreased photosynthesis in 8 cultivars of peanut by a 2.5-hour ethylene exposure (1,150 $\mu g\ m^{-3}$) was observed, and ranged from 10 to 35% inhibition (Pallas and Kays, 1982). Leaf age was not a factor in this response. Stomatal conductance was reduced in peanut leaves treated with 1,150 $\mu g\ m^{-3}$ for 2.5 and 6 hours, with stomatal closure being greater on the lower surface of the leaf. Stomatal opening correlated with recovery in photosynthesis.

Tobacco (*Nicotiana tobaccum* L.) required higher concentrations of ethylene than peanut or soybean to induce similar photosynthetic effects (Squier *et al.*, 1985). Photosynthesis in tobacco plants treated with 589 $\mu g\ m^{-3}$ remained at near control levels through the first photoperiod (0800 to 1600 hr), but declined to about 40% of that in controls by the end of the 28-hour treatment. In plants exposed to 1,150 and 2,300 $\mu g\ m^{-3}$, photosynthesis declined immediately upon exposure to ethylene, and continued to decline to less than 20% of controls by the end of the experiment.

Green ash (*Fraxinus pennsylvanica* L.) was not as affected by ethylene as soybean, peanut and tobacco. Slight decreases in photosynthesis were observed immediately after initiation of treatment with 281 and 589 $\mu g\ m^{-3}$ ethylene, but ash seedlings retained approximately 90% of the control photosynthetic rate through the course of the experiment (Squier *et al.*, 1985).

Photosynthesis in corn (*Zea mays* L.) was not affected by concentrations up to 4,600 $\mu g\ m^{-3}$ (Squier *et al.*, 1985).

Exposure of potato (*Solanum tuberosum* L.) leaves to 575 to 1,150 $\mu g\ m^{-3}$ reduced net carbon assimilation by 10 to 18% (Govindarajan and Poovaiah, 1982). Concentrations of ethylene in excess of 1,150 $\mu g\ m^{-3}$ did not further affect the response. The initial effect was observed after a 1.5- to 2-hour lag period. As stomatal aperture was not affected by ethylene in this study, the ethylene likely interfered with CO_2 assimilation in a manner other than by stomatal control, however, activity of RuBP-carboxylase was not altered by the ethylene treatment.

Ethylene concentrations up to $1.15 \cdot 10^8\ \mu g\ m^{-3}$ did not affect air flow through the stomates of corn seedlings (Pallaghy and Raschke, 1972). While stomatal effects were apparent in the studies of Squier *et al.* (1985), direct effects of ethylene on carbon assimilation may also have occurred. High ethylene concentrations (11,500 $\mu g\ m^{-3}$) have been shown to inhibit photosynthetic electron transport in the light reactions in soybean, thereby reducing available cellular energy for carbon assimilation (Wullschleger *et al.*, 1992).

Photosynthesis in Jerusalem artichoke (*Helianthus tuberosus* L.), sunflower (*Helianthus annuus* L.) and sweet potato (*Ipomoea batatas* L.) was also inhibited by 1,150 $\mu g\ m^{-3}$ ethylene, however, the effect was less than that observed in peanut (Pallas and Kays, 1982). There was no effect of 1,150 $\mu g\ m^{-3}$ ethylene (for 2.5 hours) on photosynthesis in green bean (*Phaseolus vulgaris* L.), scarlet runner bean (*P. coccineus* L.), pea, Irish potato (*Solanum tuberosum* L.),

TABLE XI

EFFECT OF ETHYLENE ON RESPIRATION AND ALCOHOL DEHYDROGENASE ACTIVITY[†]

Species	Ethylene ($\mu g \; m^{-3}$)	Exposure Duration	Respiration (% of Control)	ADH Activity (% of Control)
Pea (*Pisum sativum*)	11.4	48 hours	180	124
	113.5	48 hours	190	407
	1,135	48 hours	210	201

†   Data from Ageev *et al.* (1996)

sensitive plant (*Mimosa pudica* L.) and white clover (*Trifolium repens* L.).

The study by Squier *et al.* (1985) is one of the few which have employed treatment concentrations which are comparable to those found in ambient air in urban and industrial areas. While the treatments used were short-term continuous exposures, which did not follow the patterns found in most urban areas (morning and afternoon peaks), the treatment concentrations did approximate those found during the light period when photosynthesis and carbon assimilation is active. These results strongly indicate that ethylene concentrations in the range of 112 to 2,300 $\mu g \; m^{-3}$ will affect photosynthesis, and hence growth, of some plant species.

7.2.3 Respiration

Ethylene effects on dark respiration (CO_2 release from plants in the dark) and activity of the individual enzymes in the pentose phosphate pathway in 8-day-old pea seedlings exposed to 11.4, 113.5 and 1,135 $\mu g \; m^{-3}$ ethylene for 48 hours were reported by Ageev *et al.* (1996); these results are summarized in Table XI. At 11.4 $\mu g \; m^{-3}$, CO_2 evolution from pea seedlings increased relative to CO_2 evolution from peas kept in an ethylene-free chamber. Since this level of ethylene is generally considered to occur naturally in ambient air, this treatment is considered to be the control and the basis of comparison of the effects of ethylene at higher concentrations. At 113.9 $\mu g \; m^{-3}$, CO_2 evolution remained the same as at 11.4 $\mu g \; m^{-3}$ (significantly higher than in the ethylene-free treatment), while alcohol dehydrogenase (ADH) enzyme activity increased by a factor of 4. Increased ADH activity is indicative of a shift in plant metabolism resulting from anaerobic conditions (reduced oxygen availability). Although the precise role is unknown, ethylene plays a role in responses of plants to anaerobic conditions. Taken together, the effects of 113.9 $\mu g \; m^{-3}$ are considered to be of relevance in deriving a guideline for ethylene.

7.2.4   Plant Growth

Ethylene exposure may affect root growth, shoot growth, or other processes involving roots and shoots (e.g. interactions between roots and microorganisms). The studies describing these effects are summarized in Table XII.

Root elongation in 48-hour-old corn seedlings was inhibited at ethylene concentrations of 115 $\mu g \; m^{-3}$ and above (Whalen and Feldman, 1988). Ethylene was applied to the entire

TABLE XII
ETHYLENE EFFECTS ON ROOT AND SHOOT GROWTH

Species	Ethylene (µg m^{-3})	Exposure Duration	Effect	Reference
Corn (*Zea mays*)	≥115	24 hours	Inhibition of root growth	Whalen and Feldman (1988)
	115	7-14 days	No effect on root growth	Jackson *et al.* (1981)
	115	14 days	Inhibition of leaf growth	Jackson *et al.* (1981)
	1,150	7-14 days	Inhibition of root growth	Jackson *et al.* (1981)
	5,750	7-14 days	Inhibition of root growth	Jackson *et al.* (1981)
Barley (*Hordeum vulgare*)	≤11,500	21 days	Inhibition of root growth	Crossett and Campbell (1975)
Tomato (*Lycopersicon esculentum*)	23	1-4 days	Promotion of root growth	Konings and Jackson (1979)
	58	1-4 days	Inhibition of root growth	Konings and Jackson (1979)
Rice (*Oryza sativa*)	23 to 173	24 hours	Promotion of root growth	Konings and Jackson (1979)
	1,150	24 hours	Inhibition of root growth	Konings and Jackson (1979)
	1,135	3 days	Promotion of coleoptile growth	Pearce *et al.* (1992)
	1,135	6 days	Promotion of coleoptile growth	Lee and Chu (1992)
White Mustard (*Sinapis alba*)	58 to 1,150	24 hours	Inhibition of root growth	Konings and Jackson (1979)
Pea (*Pisum sativum*)	23 to 46	7 days	Threshold for inhibition of growth and geotropism in epicotyl and root	Goeschl and Kays (1975)
	81	3 weeks	Reduced root nodulation	Lee and LaRue (1992b)
	253	3 weeks	Reduced root nodulation	Lee and LaRue (1992b)
	518	3 weeks	Reduced root nodulation	Lee and LaRue (1992a)
	11,500	7 weeks	Reduced root nodulation	Goodlass and Smith (1979)
Bean (*Phaseolus vulgaris*)	92 to 184	7 days	Threshold for inhibition of root and shoot growth	Goeschl and Kays (1975)
Clover (*Trifolium repens*)	81	3 weeks	Reduced root nodulation	Lee and LaRue (1992b)
	11,500	4 weeks	Reduced root nodulation	Goodlass and Smith (1979)
Soybean (*Glycine max*)	518	3 weeks	No effect	Lee and LaRue (1992b)
Peanut (*Arachis hypogaea*)	46-368	7 days	Threshold for inhibition of root and shoot growth	Goeschl and Kays (1975)
Echinochloa oryzoides	1,135	3 days	Inhibition of mesocotyl growth	Pearce *et al.* (1992)
Cotton (*Gossypium hirsutum*)	184 to 368	7 days	Threshold for inhibition of root and shoot growth	Goeschl and Kays (1975)

germinating corn seed in a sealed test tube. Inhibition occurred within 20 minutes after initial exposure, and growth returned to normal within 15 minutes of removal of ethylene. The response saturated at 6,900 µg m^{-3}. Barley (*Hordeum vulgare* L.) roots showed significantly reduced growth following a 21-day treatment with up to 11,500 µg m^{-3} ethylene (Crossett and Campbell,

1975). Only under conditions where ethylene builds up to these high levels in the soil would barley be affected. These circumstances are most likely to occur naturally under extreme conditions (e.g. in flooded soils) rather than as a result of human activity. Ethylene at 1,150 and 5,750 μg m^{-3} in the gas stream bubbled though the nutrient medium for 7 to 14 days of hydroponically grown corn (4-leaf stage) inhibited seminal root elongation and dry weight accumulation (Jackson *et al.*, 1981). Ethylene at 115 μg m^{-3} did not have a statistically significant effect on corn root growth.

Tomato (*Lycopersicon esculentum* Mill.) root elongation was stimulated by 15% following a 24-hour exposure to 23 μg m^{-3} ethylene (Konings and Jackson, 1979); root elongation was also increased relative to control by 2, 3 and 4-day exposures to 23 μg m^{-3} ethylene. Significant inhibition of root elongation occurred at concentrations of 58 μg m^{-3} and above. In rice (*Oryza sativa* L.), growth of ethylene-treated roots increased following 24-hour exposures to 23, 58 and 173 μg m^{-3} ethylene. Growth was inhibited at 1,150 μg m^{-3} ethylene. Roots of white mustard (*Sinapis alba* L.) were not affected by exposure to 23 μg m^{-3} for 24 hours, however, root elongation was significantly inhibited (by 20%) at 58 μg m^{-3}, by 50% at 173 μg m^{-3}, and by 77% at 1,150 μg m^{-3}.

Interactions between plant roots and soil mycorrhyzae are important to the health and growth of plants. Ethylene has been observed to affect this association, however, the effects were observed at concentrations at or above 92,000 μg m^{-3} ethylene (Tosh *et al.*, 1994). The effects of ethylene at levels 100 to 1,000-fold lower (as would be found in ambient air) were not determined. Root growth of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) seedlings treated with ethephon to generate ambient soil concentrations of 7 to 575 μg m^{-3} ethylene was promoted at concentrations of 12 to 58 μg m^{-3} ethylene, was not affected between 58 and 173 μg m^{-3}, and was inhibited above 173 μg m^{-3} (Graham and Linderman, 1981). Mycorrhizal infection of the roots was not affected by ethylene (ethephon) treatment, however, root infections by pathogenic fungi were increased at 115 μg m^{-3} ethylene. Ethylene treatments were not continuous, since ethephon degrades rapidly within plant tissues during the first few days after application (Graham and Linderman, 1981; Foster *et al.*, 1992). In some cases, a second application of ethephon to the soil was required to increase the ethylene concentration applied to the roots. It is unclear whether ethylene release from ethephon occurred in the soil, or was a function of degradation within the root cells. This complicates interpretation of this data, and this study is not included among those summarized in Table XI, nor is it used in the derivation of an ethylene guideline.

Nodulation of pea roots is inhibited by ethylene (Goodlass and Smith, 1979; Lee and LaRue, 1992b). Treatment of roots for seven weeks with 11,500 μg m^{-3} ethylene, beginning when the plants were 4 weeks old, reduced nodulation by 75% (Goodlass and Smith, 1979). Root growth was affected only slightly, but shoot growth was reduced by 30 to 50%. Continuous treatment from seeding to harvest (21 days after seeding) of the pea cultivar Sparkle with 81 μg m^{-3} ethylene reduced the number of nodules per plant from 306 (in control plants) to 145 (Lee and LaRue, 1992b), and from 302 to 17 per plant following exposure to 518 μg m^{-3} ethylene for 3 weeks (Lee and LaRue, 1992a). Nodule number was reduced to 50 per plant following a 21-day exposure to 253 μg m^{-3} ethylene, and nodules were almost completely absent from plants exposed to a 518 μg m^{-3} ethylene treatment (Lee and LaRue, 1992b). Root growth was not as sensitive to ethylene, being reduced by 50% in length and 31% in dry weight. Similar results

were obtained using the other pea genotypes Rondo, Sparkle E135F (a mutant which forms small ineffective nodules), the hypernodulating genotype Rondo nod-3 (Lee and LaRue, 1992b), and the low nodulation mutant R82 (Lee and LaRue, 1992a). Thus, nodulation responses are more general, and not restricted to one pea genotype. Clover was found to be more sensitive than pea (Lee and LaRue, 1992b), with nearly complete inhibition of nodulation occurring at and above 81 $\mu g \ m^{-3}$ ethylene, while root growth was reduced only slightly. Root growth in soybean was also reduced slightly by up to 518 $\mu g \ m^{-3}$ ethylene, while nodulation was not reduced in this species (Lee and LaRue, 1992b). Treatment of soybean roots with ethephon at levels which significantly reduced shoot growth and plant wet and dry weights did not reduce nodulation (Hunter, 1993). At very high levels of ethephon (1,000 μM), root growth, lateral root number and nodulation were reduced; however, in this study the effect of ethephon (ethylene) on nodulation was likely non-specific (i.e. reduced nodulation was an indirect effect).

Mutants of *Rhizobium leguminosarum* bv. *viciae* which are reduced in their ability to effectively induce nodulation in vetch (*Vicia sativa* spp. *nigra*) were even less able to induce nodulation in the presence of ethylene (van Workum *et al.*, 1995). Ethylene removal by addition of AVG (1-aminoethoxyvinyl glycine; an ethylene biosynthesis inhibitor) increased effective nodulation in vetch (van Workum *et al.*, 1995) and in *sym-5* mutants of Sparkle pea (Fearn and LaRue, 1991). However, while AVG treatment of soybean reduced ethylene production, it did not affect inoculation by *Bradyrhizobium japonicum* (Suganuma *et al.*, 1995). As with many other plant responses involving ethylene, the role of ethylene in nodulation appears to vary by species (both plant and microorganism).

Mesocotyl, but not coleoptile, growth in barnyard grass (*Echinochloa oryzoides* [Ard.] Fritsch) seedlings was inhibited by 24% by treatment with 1,135 $\mu g \ m^{-3}$ ethylene for 3 days (Pearce *et al.*, 1992). When applied to seedlings of rice, this concentration increased coleoptile extension by 61% (Pearce *et al.*, 1992). Stimulation of coleoptile growth in rice in response to 1,150 $\mu g \ m^{-3}$ ethylene was observed by Lee and Chu (1992), and this increase was coincident with increases in polyamine (spermidine and putrescine) content. Since concentrations lower than 1,150 $\mu g \ m^{-3}$ were not used, these data are not relevant in the derivation of an ethylene guideline.

Leaf growth in corn (4-leaf stage) was inhibited by bubbling 115 $\mu g \ m^{-3}$ ethylene through the nutrient medium for 14 days (Jackson *et al.*, 1981). Higher concentrations (1,150 and 5,750 $\mu g \ m^{-3}$) further reduced growth. These data are not used in determining an ethylene guideline, since root fumigations at these levels would be very rare under field conditions.

In an attempt to understand ethylene effects on physiological mechanisms, growth of roots and stems in pea, peanut, bean, and cotton (*Gossypium hirsutum* L.) seedlings in response to a range of ethylene concentrations were investigated by Goeschl and Kays (1975). Pea epicotyl geotropism, epicotyl elongation, root elongation, epicotyl diameter, root geotropism and root diameter exhibited half-maximal responses at 109, 124, 351, 368, 380, 426 $\mu g \ m^{-3}$, respectively. The thresholds for these responses were in the range of 23 to 46 $\mu g \ m^{-3}$. The half-maximal concentrations inhibiting bean hypocotyl elongation, hypocotyl diameter, and root elongation were 380, 449, and 529 $\mu g \ m^{-3}$; the thresholds for these responses were between 92 and 184 $\mu g \ m^{-3}$. The threshold levels for hypocotyl elongation, hypocotyl diameter and root elongation in peanut seedlings were between 46 and 368 $\mu g \ m^{-3}$. Higher levels of ethylene were required to

elicit half-maximal responses in cotton: 644 µg m^{-3} for cotton hypocotyl elongation, 702 µg m^{-3} for root elongation, and 1,553 µg m^{-3} for hypocotyl diameter, with thresholds between 184 and 368 µg m^{-3}. Some responses (e.g. geotropism in hypocotyls of bean, cotton and peanut) were not observed at concentrations of up to 11,776 µg m^{-3}. Although conditions which are very artificial (treatment of very young etiolated seedlings) relative to those found in field conditions were used, these results indicate that some plants respond to very low levels of ethylene.

Abeles and Heggestad (1973) investigated the effects of ethylene on growth, development and reproduction in a number of species. Bean, African violet (*Viola* sp.), cucumber (*Curcurbita pepo*), marigold (*Tagetes erecta* L.), soybean, spring wheat (*Triticum aestivum* L.), petunia (*Petunia nyctaginiflora* Juss), honey locust (*Gleditsia triancanthos* L.), and tomato were grown in sealed fumigation chambers and exposed to concentrations of ethylene observed in the ambient air in Washington DC. While there was some variability in the responses among species, the general conclusion was that the threshold level for an ethylene effect was 12 µg m^{-3}, with a half-maximal response between 115 and 575 µg m^{-3}, and saturation above 1,150 µg m^{-3}. Levels observed in the air in Washington DC were therefore expected to have an effect on area vegetation. However, as this study was not properly replicated and statistically analyzed, these data can only be used as background information in derivation of an ambient air quality guideline for ethylene.

Ethylene levels rose to an estimated 115 to 230 µg m^{-3} in a sealed growth chambers used for growing wheat (Martin and Sinnaeve, 1987); presumably these levels originated from the wheat plants. Growth was described as "very poor" and improved dramatically following the installation of an ethylene removal system containing acid permanganate on activated alumina. Recirculation of the chamber air through the ethylene trap lowered ethylene levels to below the limit of detection of 12 µg m^{-3}. Growth of the wheat improved markedly within 48 hours of installing the purification system.

Ethylene emission from landfills may also negatively affect plant growth. Ethylene escaping from vent pipes, and through the covering soil, was proposed as a contributing factor to poor plant growth on the covered Gin Drinkers' Bay landfill, Hong Kong (Wong and Yu, 1989b). Carbon dioxide, oxygen, methane and soil extractable lead also negatively affected plant growth. The amounts of ethylene in the ambient air, and in the soil, were not given.

7.2.5 Abscission and Senescence

The longevity of cut flowers may be affected by ethylene (Table XIII), and ethylene effects on flowers are therefore an important economic consideration in the horticulture industry. However, the effects of ethylene on senescence and abscission are complex, and not fully understood. Flower sensitivity (abscission and senescence of the flower) varies by plant family, with some families being very sensitive (e.g. orchid, geranium, mint, and mallow families) relative to others (e.g. composite, parsley, and lily families) (Woltering and Van Doorn, 1988). Additionally, there may be large differences among plant species within a family, and even cultivars within a single species, with respect to sensitivity to ethylene and senescence and abscission. A ranking of flower sensitivity in 93 species representing 22 plant families is presented in Woltering and Van Doorn (1988). As ethylene levels used to assess flower

TABLE XIII
EFFECTS OF ETHYLENE ON ABSCISSION AND SENESCENCE

Species	Ethylene ($\mu g\ m^{-3}$)	Exposure Duration	Effect	Reference
Carnation	35 to 69	48 hours	Increased flower senescence	EPA (1978)[†]
(*Dianthus*	58	48 hours	Increased flower senescence	Woltering and Harkema (1987)
caryophyllus)	115	48 hours	Increased flower senescence	Woltering and Harkema (1987)
	≥115	24 hours	Increased flower senescence (cv. White Sim)	Woltering *et al.* (1993)
	≥265	24 hours	Increased flower senescence (cv. Chinera)	Woltering *et al.* (1993)
	≥345	24 hours	Increased flower senescence (cv. Epomeo)	Woltering *et al.* (1993)
	575	12 hours	Increased flower senescence	Woltering and Harkema (1987)
	575	12 hours	Increased flower senescence	EPA (1978)
Morning glory (*Ipomoea* *tricolor*)	12	≥1 hour	Threshold for increased petal senescence	Hanson and Kende (1975)
	115	≥1 hour	Half-maximal exposure for petal senescence	Hanson and Kende (1975)
	11,500	≥1 hour	Saturation for petal senescence	Hanson and Kende (1975)
	≥1,150	20 to 40 minutes	Increased flower fading	Kende and Baumgartner (1974)
Rose (*Rosa* spp.)	23	2 days	Inhibition of flower opening (cv. Lovely Girl)	Reid *et al.* (1989)
	≤1,1	2 days	Inhibition of flower opening (cv. Gold Rush)	
Begonia	173	10 days	Increased flower abscission and reduced flower quality	Nowak and Fjeld (1993)
Easter lily (*Lilium longiflorum*)	58	77 days	Flower stunting and distortion	Blankenship *et al.* (1993)
Orchid	46 to 115	8 hours	Increased flower senescence	EPA (1978)
	2 to 23	24 hours	Increased flower senescence	
Pecan (*Carya illinoensis*)	115	14 days	Increased shuck dehiscence (cv. Desirable)	Kays *et al.* (1975)
	288	14 days	Increased shuck dehiscence (cv. Big Z)	
Ficus (2 species)	575	48 hours	5% Defoliation	Turner *et al.* (1988)
	19,550	48 hours	20% to 60% Defoliation	
English ivy (*Hedera helix* L.)	11,500		Increased leaf senescence	Horton and Bourguoin (1992)

† EPA (1978) = Environmental Protection Agency (1978)

sensitivity were relatively high (3,405 $\mu g\ m^{-3}$) over a short treatment period (22 to 24 hours), thus these data cannot be directly used in the derivation or validation of an ethylene guideline. However, other research more relevant to environmental exposures is available, and is presented

below.

Senescence of carnation (*Dianthus caryophyllus*) flowers in response to ethylene treatment was investigated by Woltering *et al.* (1993). Three cultivars of cut carnations were exposed to 12 to 12,650 μg m^{-3} ethylene in sealed chambers for 24 hours. Increased senescence of White Sim was observed above 115 μg m^{-3} ethylene, Chinera became senescent at 265 μg m^{-3}, and Epomeo at 345 μg m^{-3} ethylene. Irreversible wilting (senescence) of cut carnation flowers increased after a 48-hour exposure to 58 μg m^{-3} ethylene, a 24-hour exposure to 115 μg m^{-3} ethylene, and a 12-hour exposure to 575 μg m^{-3} (Woltering and Harkema, 1987). Confirmation of a proposed mathematical relationship among irreversible wilting, exposure time and ethylene concentration was not possible, therefore, this data (Woltering and Harkema, 1987) was not used in assessing or developing an ethylene guideline. Levels of up to 207 μg m^{-3} ethylene in the Denver metropolitan area did not affect carnation marketability since ethylene did not appear to affect the flowers while kept in cold storage (Hanan, 1973). However, longevity of flowers kept at room temperature is expected to be reduced during a period of severe pollution (Hanan, 1973).

Short (20- to 40-minute) exposures of excised morning glory (*Ipomoea tricolor*) flowers to concentrations of 1,150 μg m^{-3} ethylene and above hastened flower fading relative to controls (Kende and Baumgartner, 1974).

Flower opening in rose cultivars (*Rosa* sp.) may be accelerated, inhibited, or unaffected in response to an exposure of 575 μg m^{-3} ethylene (Reid *et al.*, 1989). Flower distortion and abscission also occurred in some cultivars. Cultivars which were affected by ethylene were sensitive to low concentrations of the gas. Flower opening in Lovely Girl, one of the most sensitive genotypes, was inhibited by 23 μg m^{-3} ethylene, with maximum inhibition observed at 138 μg m^{-3} ethylene. The cultivar Gold Rush was not affected by ethylene at concentrations up to and including 1,150 μg m^{-3} (Reid *et al.*, 1989).

Rolling of petal rib segments excised from morning glory flowers has been used as a model to study flower senescence (Hanson and Kende, 1975). Treatment of rib segments with 12 μg m^{-3} increased the extent of rolling a small amount relative to the controls (exposed to air only). The onset of rolling occurred 1 hour earlier than the onset of rolling in the controls. Increasing ethylene concentrations up to 11,500 μg m^{-3} increased the extent of rolling (half-maximal response at 115 μg m^{-3}), although the timing of the initiation of rolling was not altered by ethylene concentration. Early induction and increased rolling in response to ethylene closely paralleled the behaviour of the rib tissue during fading of the intact flower. Continuous treatment was not required. Rib tissues exposed for 1 to 1.5 hours exhibited early onset of rolling, and the extent of rolling was increased relative to controls, although the maximum rolling response in short-term treatments was less than that observed in continuous treatments. Thus, short exposures to elevated ethylene levels may be sufficient to alter flower longevity in morning glory.

The keeping quality of potted flowers is also of considerable economic importance. Flower number and quality were reduced in two varieties of Begonia (*Begonia* x *cheimantha* and *B.* x *hiemalis*) following a 10-day exposure to 173 μg m^{-3} ethylene, although one genotype (*B.* x *hiemalis*) was more sensitive than the other (Nowak and Fjeld, 1993). Flower abscission was the primary cause of lower flower numbers, since flower bud development was relatively unaffected. Partitioning of ^{14}C (supplied to the plant as ^{14}CO$_2$) into the flower and flower buds was reduced

by ethylene treatment, however, it is not clear if this was the primary mode of action of ethylene, or was a secondary effect following the onset of senescence and abscission. Long-term (77-day) exposure to 58 µg m^{-3} rendered Easter lily (*Lilium longiflorum* Thunb.) unmarketable due to severe stunting of growth and distortion of the flower (Blankenship *et al.*, 1993). Easter lilies tolerated chronic ethylene levels of up to 12 µg m^{-3}. The treatment concentrations used in these experiments (Blankenship *et al.*, 1993; Nowak and Fjeld, 1993) are comparable to those found in urban areas. These experiments strongly suggest that the health of potted plants may be adversely affected by ethylene in urban settings.

Flowering (inhibition of flowering, or reduction in flower size) in petunia has been suggested as a possible means of monitoring ethylene levels in the environment (Posthumus, 1980). However, the response was poorly characterized, and a quantitative relationship between ethylene exposure and plant response was not presented.

Drying and bleaching of orchid sepals was reported to occur following an 8-hour exposure to 46 to 115 µg m^{-3}, or after a 24-hour exposure to 2 to 23 µg m^{-3} (Environmental Protection Agency, 1978). These results were not substantiated with a presentation of the data, but rather appeared as part of a review article (the original reference was not included), and consequently, these data can not be used in derivation of an ethylene guideline.

Leaf senescence also increases in response to ethylene exposure. Leaf blade senescence in English ivy (*Hedera helix* L.) increased following a treatment with 11,500 µg m^{-3} (Horton and Bourguoin, 1992). This concentration is very high relative to ambient air ethylene levels, and is not useful in evaluating or proposing an ethylene guideline.

Shuck dehiscence in pecan (*Carya illinoensis* [Wang.] K. Koch) increased following a 14-day exposure to 115 µg m^{-3} in one variety, and at 288 µg m^{-3} for 14 days in a second (Kays *et al.*, 1975). Leaf and fruit abscission increased following a 14-day treatment of 863 µg m^{-3} ethylene. While pecans do not grow in Alberta, these results show that different organs respond at different concentrations of ethylene, and that abscission of leaves and fruits may occur in response to levels of ethylene occasionally found in urban environments. Defoliation of two species of *Ficus* began at 575 µg m^{-3}, with 20% (*F. stricta*) to 60% (*F. benjamina*) defoliation occurring at 19,550 µg m^{-3} (Turner *et al.*, 1988). These levels are not expected to occur under ambient conditions.

7.2.6 Effects on Fruit and Yield

Initiation of ripening following ethylene exposure is one of the classic effects of this gas (Abeles *et al.*, 1992). However, no studies describing ripening responses as a result of exposure to concentrations of ethylene expected to occur in ambient air are available.

As with senescence and abscission, there is limited data available for assessing the effects of ethylene on crop yield under ambient conditions. Ethylene effects are likely complex, depending upon environmental conditions, and vary by species and cultivar.

Removal of ethylene from air reduced the yield of canola and oat, relative to the yields of these crops grown under background ethylene levels (Table XIV) (Reid and Watson, 1985). Ethylene-free air is a highly unnatural condition, and may have negatively affected plant growth and development. Thus, for the purpose of assessing the effects of ethylene in the context of

TABLE XIV
EFFECTS OF ETHYLENE ON OAT AND CANOLA YIELD[†]

Species	Ethylene (μg m^{-3})	Exposure Duration	Effect
Oat (*Avena sativa* L. cv. Random)	0	100 days	Per plant floret number increased by 29%
	8[††]	100 days	—
	40	100 days	Per plant floret number decreased by 26%
	81	100 days	Per plant floret number decreased by 89%
	173	100 days	Per plant floret number decreased by 99%
Canola (*Brassica campestris* L. cv. Candle)	0	87 days	Per plant seed yield reduced by 65%
	12[††]	87 days	—
	40	87 days	Per plant seed yield reduced by 52%
	173	87 days	Per plant seed yield reduced by 84%
	690	87 days	Per plant seed yield reduced by 99%

[†] Data from Reid and Watson (1985)

[††] These levels are considered to represent "background" ethylene concentrations, and therefore, these levels are considered the "control" for the determination of effects of higher, and lower, ethylene concentrations.

guideline derivation, the treatment concentrations of 8 and 12 μg m^{-3} are considered to be the controls, and effects of other ethylene treatments are compared to these levels.

Canola seed yield was drastically reduced at exposures of 173 μg m^{-3} (for 87 days) ethylene and above, while oat yield dropped substantially at 81 μg m^{-3} (for 100 days) and above (Reid and Watson, 1985). While not as drastic, seed yield in both crops dropped as ethylene levels rose from 8 (oat) or 12 μg m^{-3} (canola) to 40 μg m^{-3}. Thus, 40 μg m^{-3} is considered to be the level at which a negative effect occurred for both species. This concentration is therefore considered to be the effects level for the purposes of guideline development.

8.0 EFFECTS OF ETHYLENE ON HUMAN HEALTH

As stated in the Introduction (Section 2.0), effects of ethylene on human health are not considered in this review and evaluation of ethylene effects. Ethylene is thought to affect vegetation at levels which are two to three orders of magnitude lower than levels which affect health. The levels typically found in ambient air have not been expected to directly affect human health (National Research Council of Canada, 1985). However, indirect human health effects resulting from atmospheric reactions involving ethylene may occur (reactions to photochemical smog), but discussion of these effects is beyond the scope of this document.

9.0 DATA GAPS

9.1 Ambient Ethylene Levels in Alberta

In order to determine the amount of ethylene in air in Alberta which results from urban and industrial activity, it is necessary to know the levels of ethylene in ambient air which result from natural sources (primarily vegetation). At present, the background ethylene level in Alberta is considered to be about 12 μg m^{-3}. Verification of this background level in forested, grassland, and agricultural environments is recommended. These measurements should be conducted at sites well away from anthropogenic ethylene emissions (e.g. well removed from away from roads and industrial facilities). Peak levels (daily, monthly, and seasonal peaks), and average levels (6-hour, daily, monthly, annual) should be determined.

In order to determine which areas of Alberta experience elevated levels of ethylene, and the frequency and magnitude of these elevations, a survey of ambient air ethylene concentrations in a number of locations throughout the year is required. Since the concerns about ambient air levels primarily relate to anthropogenic ethylene emissions, it is important to determine the levels of ethylene resulting from human activity. Therefore, it is recommended that ethylene levels be surveyed in Calgary and Edmonton throughout the year, under a variety of environmental conditions. Sampling and measurement of ethylene in a moderately sized city would provide information about ethylene levels in Alberta's smaller centres; Red Deer, Medicine Hat, Lethbridge, and Grande Prairie may be candidates for these measurements. As outlined above for rural environments, peak levels (daily, monthly, and seasonal peaks) and average 6-hour, daily, monthly and annual levels should be determined.

Since ethylene may also be released from various industrial facilities, ethylene levels in the vicinity of these facilities should also be determined. Of primary interest are the oil and gas processing facilities and the petrochemical operations in the province. Suggested locations are the Joffre-Prentiss area (production and use of ethylene), Sherwood Park (industrial area east of Edmonton) Fort McMurray (oilsands), and Crossfield or Waterton (large natural gas processing facilities). Since releases of ethylene from such facilities are likely sporadic, short-term events, the interval between collection of samples should be relatively short. Protocols for sampling and analysis of ethylene levels in air should be consistent with the protocols used for urban and rural sampling and analysis, which will allow direct comparison of data and results.

A recent report describing the products of combustion from flaring of sweet and sour gas shows that ethylene is released from these flares (Strosher, 1996). The effects of ethylene produced by flaring are likely to occur in the immediate vicinity of each flare. It is recommended that further characterization of emissions from flares be conducted, and that measurements of ambient ethylene levels surrounding flares be made. Depending upon the levels found, a survey for potential effects of ethylene on vegetation around flare sites may be justified.

9.2 Environmental Effects of Ethylene

For the past several years, the focus of research efforts into the effects of ethylene has been to answer the question: Does ethylene affect plant growth and development? As a result, ethylene

treatments given over short time periods have been high relative to ambient air concentrations that plants are generally exposed to over longer periods of time. This has led to the understanding that as a plant hormone, ethylene is involved in a wide range of physiological processes, leading to effects visible at the morphological and anatomical levels.

To support the development and implementation of a full ambient air quality guideline for ethylene, research must now be directed towards answering the following questions:

- ▸ for a variety of species (crops, trees, native vegetation) what are the dose-response relationships between ethylene exposure and effects?

- ▸ are plants more susceptible to ethylene exposure at particular times during growth and development?

- ▸ what effects do environmental conditions (water availability, soil salinity, pathogenic infection, previous or co-exposure to other air contaminants) have on plant susceptibility to ethylene?

Growth chambers designed specifically for fumigation studies (Diesburg *et al.*, 1989) may be of use in conducting this research. However, to be most meaningful, ethylene fumigations of plants should be conducted under field conditions. Exposure systems for field use (open-top chambers, ring fumigation systems) have been designed (Greenwood *et al.*, 1982; Heck *et al.*, 1988; Hendrey, 1993; Hendrey *et al.*, 1992; Runeckles *et al.*, 1990), and may be of use in Alberta.

The preliminary ethylene guideline in current use in Alberta (120 μg m^{-3}, 6-hour average) is applied during the period when stomates are presumed to be open (0300 hr to 2200 hr), during the May to September growing season. The assumption inherent in this application are that plants are not sensitive to ethylene exposure during the night, since stomates are closed. This assumption, using native vegetation and plants cultivated in Alberta, should be tested.

In Alberta, most plant species are dormant between October 1 through April 30, inclusive, and hence, it is assumed that they are not sensitive to ethylene exposure. This assumption should be tested using plant species which may be physiologically active during the late fall and early spring period (e.g. conifers). Additionally, higher ambient levels of ethylene during the winter may have implications for the protection of human health, and this must be taken into account should winter ethylene levels be of concern.

Little is known about ethylene effects on microorganisms. These studies should be comparatively simple to conduct, and may be easily accomplished under laboratory conditions. Investigations into ethylene effects on mosses and lichens are also required.

TABLE XV
ALBERTA AMBIENT AIR ETHYLENE GUIDELINES (INTERIM)

Interim Ethylene Guideline	Averaging Period	Daytime Application Period	Seasonal Application Period
120 µg m^{-3}†	6 hours	0300 to 2200 hours	May 1 through September 30, inclusive
50 µg m^{-3}	30 days	0300 to 2200 hours	May 1 through September 30, inclusive

† This is the preliminary guideline currently used in Alberta.

10.0 ALBERTA AMBIENT AIR ETHYLENE GUIDELINES (INTERIM)

The recommended ethylene ambient air quality guidelines, for implementation on an interim basis, are presented in Table XV. These recommendations are made based on the following rationale.

10.1 Suitability of Existing Data for Use in Developing an Ethylene Guideline

The existing scientific literature on ambient ethylene levels and on the effects of ethylene on the environmental receptors is generally of good quality, however, it is limited in quantity and scope. The primary deficiency is that there have been few studies on the effects of ethylene at concentrations expected to occur in ambient air (<1,150 µg m^{-3}). Those which do exist describe effects in a limited number of species, many of which are not native or grown in Alberta. As a result, there is insufficient data in the literature of direct relevance to Alberta to allow for the development of a full guideline for ethylene. The data presented in this report are therefore used to evaluate Alberta's existing preliminary ethylene guideline (120 µg m^{-3}, 6-hour averaging period) and to determine if an interim guideline for a longer period of exposure is required.

10.2 Ambient Levels and Ethylene Effects on Vegetation

Abeles and Heggestad (1973) suggested that the threshold for a plant response to ethylene is approximately 12 µg m^{-3}, with half-maximal responses occurring in the range of 115 to 575 µg m^{-3}. Concentrations approaching 115 µg m^{-3} have been observed in Calgary (Reid and Watson, 1981), and levels approaching 805 µg m^{-3} in other urban environments (Abeles and Heggestad, 1973). Ambient air ethylene concentrations above background may be expected to occur in the vicinity of industrial facilities outside of urban areas (Joffre and Fort McMurray areas), however, these measurements have not been made. Of particular relevance to Alberta is the study by Reid and Watson (1985) which described reduced yield in canola and oat (crops which are of economic importance in the province) as a consequence of ethylene treatment at relatively low levels (40 to 173 µg m^{-3}) .

Reid and Watson (1981) propose that an ambient level of 40 µg m^{-3} be established as an Alberta guideline. Abeles and Heggestad (1973) suggest that 12 µg m^{-3} is the threshold for a plant response to ethylene. These values are of the same magnitude as some of those shown to have an effect: petal senescence occurred in morning glory exposed to 12 µg m^{-3} for 7 hours

(Hanson and Kende, 1975); petal senescence in some rose varieties increased at 23 µg m^{-3} ethylene for 2 days (Reid *et. al.*, 1989); nodulation in pea and white clover was reduced at 81 µg m^{-3} ethylene for 21 days (Lee and LaRue, 1992b); and soybean and peanut photosynthesis were significantly decreased at 112 µg m^{-3} ethylene for 28 hours (Squier *et. al*, 1985). Appendix I also contains data which show that some plant species are not affected by these levels, at least for the measurement endpoints investigated.

10.3 Validation of the Preliminary Alberta Ethylene Guideline

The data describing effects of short-term ethylene exposure on vegetation are presented in Appendix 1 and Figure 1. Exposure to 1,150 µg m^{-3} for 6 hours or less (study 6; Pallas and Kays, 1982) reduced photosynthesis in peanut, Jerusalem artichoke, sunflower and sweet potato. The threshold for inhibition of root elongation in corn seedlings occurred at 115 µg m^{-3} ethylene in a 24 hour exposure (study 7; Whalen and Feldman, 1988). While Goeschl and Kays (1975; study 22) presented data showing that root growth in rice, white mustard and tomato seedlings was affected at low levels of ethylene (23 to 58 µg m^{-3}), the treatment conditions were very artificial (root fumigation in sealed chambers). Similarly, reduced flower longevity in morning glory was inferred by Hanson and Kende (1975; study 16) following their observation of increased rib rolling in excised flower petals exposed to 12 µg m^{-3} for 7 hours. All of these experiments were technically well performed, however, these studies were not used in the validation of the guideline due to the highly artificial conditions used.

The data regarding short-term ethylene effects suggest that exposure of vegetation to a level of 120 µg m^{-3} ethylene for a short period of time would not have an adverse effect (Fig. 1). Therefore, the currently used preliminary guideline level of 120 µg m^{-3} (6-hour running average, applied during the growing season, daytime period of 0300 to 2200 hr) is judged protective, and is recommended for continued use on an interim basis. At the completion of the studies discussed in *Section 10.2 - Environmental Effects of Ethylene*, a reevaluation of this interim level is required, and establishment of a full ethylene guideline may be possible.

10.4 Derivation of an Interim 30-Day Ethylene Guideline

Exposure to levels lower than 120 µg m^{-3} for longer periods of time may have adverse effects on plant growth and development. Data demonstrating ethylene effects resulting from long-term exposures are presented in Appendix 1 and Figure 2.

The reduced yields in canola and oat resulting from long-term exposure to 40 µg m^{-3} in growth chambers (study 21; Reid and Watson, 1985) demonstrates that a long-term ethylene guideline is required. These crops are of major economic importance in Alberta, and are grown in the vicinity of ethylene sources (e.g. petrochemical processing facilities near Joffre AB). Flowering of Easter lily was adversely affected following a 77-day treatment with 58 µg m^{-3} (study 18; Blankenship *et al.*, 1993). While Easter lily is not a field crop, this is a whole-plant response to whole-plant fumigation, a realistic exposure regime in the field. Other studies (study 20; Goeschl and Kays, 1975; and study 22; Konings and Jackson, 1979) which demonstrate an ethylene effect below 50 µg m^{-3} are the result of treatments under artificial conditions such as
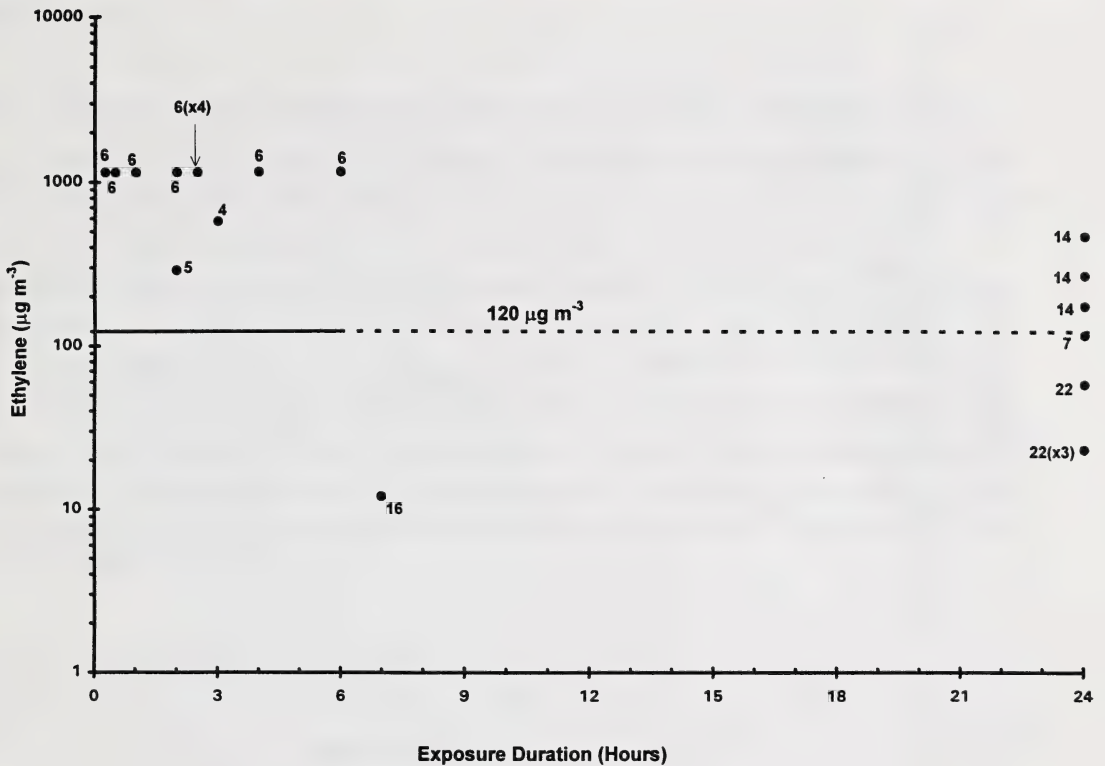
FIGURE 1. Validation of the preliminary 6-hour preliminary ethylene guideline, for application during the growing season (May 1 through September 30, inclusive). Data included in this figure are from studies which present data on short-term ethylene exposures (up to and including 24 hours in duration). Numbers beside each data point indicates the study number (Appendix 1). Numbers in parentheses (e.g. x4) indicate the number of overlapping points.

treatment in the dark for 60 hours (study 20; Goeschl and Kays, 1975) and fumigation of roots in sealed chambers (study 22; Konings and Jackson, 1979). Depending upon the cultivar, cut rose flowers may be sensitive to ethylene at low levels (23 µg m^{-3} for 2 days), or be tolerant of ethylene exposure (study 15; Reid *et al*., 1989).

While the entire database presented in Figure 2 is considered in the development of a long-
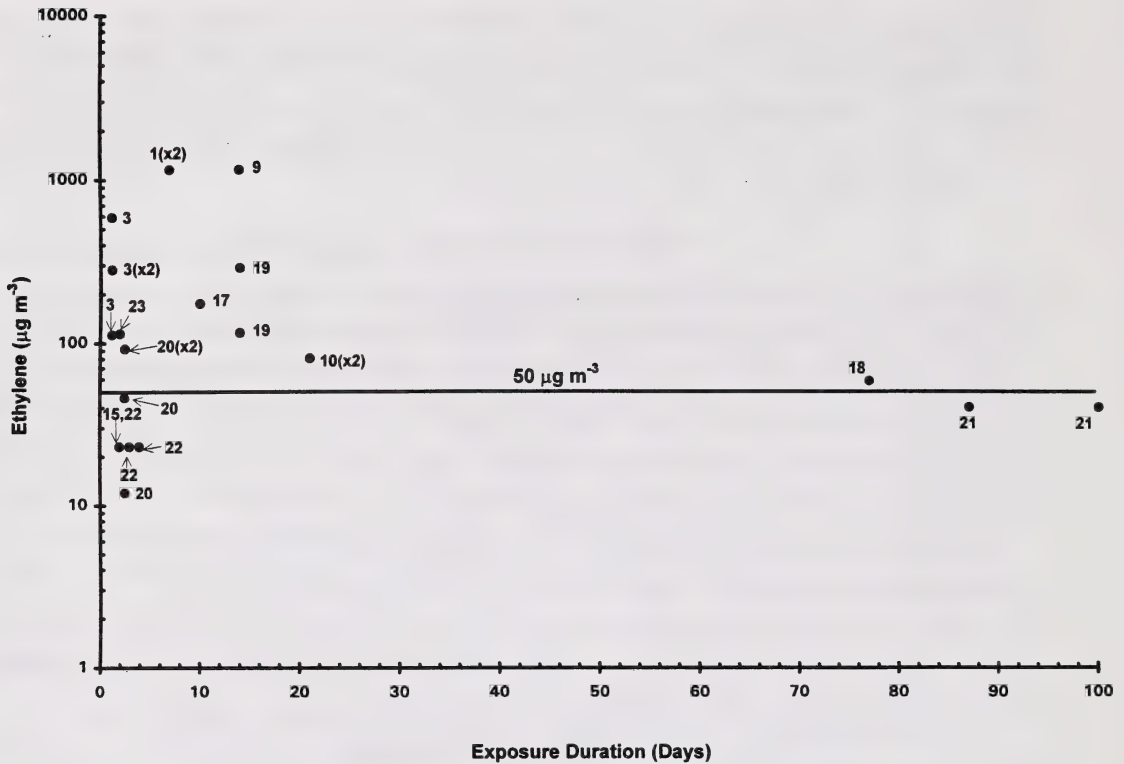
FIGURE 2. Derivation of the 30-day interim ethylene guideline for application during the growing season (May 1 through September 30, inclusive). Data included in this figure are from studies which present data on ethylene exposures of greater than 24 hours in duration. Numbers beside each data point indicates the study number (Appendix 1). Numbers in parentheses (e.g. x2) indicate the number of overlapping points.

term ethylene guideline, the oat and canola data presented by Reid and Watson (1985) is the most relevant to guideline derivation. Since these experiments were conducted in growth chambers, and plants are generally more sensitive to atmospheric contaminants under growth chamber conditions relative to ambient conditions, a guideline established at the 40 µg m^{-3} level would likely be overly protective. An interim ambient air ethylene guideline of 50 µg m^{-3} (30-

day running average, applied during the May to September growing season) is therefore recommended.

10.5   Monitoring for Compliance and Environmental Effects of Ethylene Exposure

Ambient air quality monitoring is required in the vicinity of facilities which emit ethylene. The monitoring protocol must be capable of providing the data required to determine if facilities are in compliance with the ethylene interim guidelines (e.g. calculation of 6-hour and 30-day running averages). The monitoring program will be evaluated by Alberta Environmental Protection during the process of granting operating approvals or renewals. Each monitoring program will use appropriate sampling and analytical technology, and include appropriate QA/QC protocols. The effects most likely to be observed should these interim guidelines be exceeded are: a decrease in the longevity of garden and cut flowers; decreased photosynthesis, and therefore growth; and decreased seed yields in cereal and oilseed crops. In order to determine if these effects do occur following exposure to ethylene, a receptor-based monitoring program is required. Development and operation of such a monitoring program would be most successful following discussions among all affected stakeholders (industry, agricultural community, local residents, government, etc.).

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12.0 LITERATURE NOT CITED

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SUMMARY OF ETHYLENE EFFECTS ON VEGETATION

Studies in **Bold-Face Type** are used in deriving the proposed Alberta Ambient Air Quality Ethylene Guidelines (Interim), and are included in Figure 1 or 2. The remaining studies are presented for comparative purposes.

Study No.	Reference	Species Description	Ethylene (μg m^{-3})	Exposure Duration	Ethylene Treatment	Measurement Endpoint	Effect or No Effect
1	**Egley (1980)**	**Redroot Pigweed (*Amaranthus retroflexus* L.). Seeds.**	**1,150**	**7 days**	**In flasks, kept in dark**	**Germination**	**Increased by 2.6-fold.**
1	**Egley (1980)**	**Cocklebur (*Xanthium pensylvanicum* Wallr.). Seeds.**	**1,150**	**7 days**	**In flasks, kept in dark**	**Germination**	**Increased by 2.7-fold.**
2	Baxter *et al.* (1994)	Redgrass (*Themeda triandra*). Seeds.	1.15 to 1,150,000	10 days	In sealed flasks	Germination	No Effect.
3	**Squier *et al.* (1985)**	**Soybean (*Glycine max* L). Seedlings.**	**112**	**28 hours**	**Fumigation**	**Photosynthesis**	**20% reduction. LOEC†.**
3	**Squier *et al.* (1985)**	**Peanut (*Arachis hypogaea* L. cv. Jumbo Virginiana). Seedlings.**	**281**	**28 hours**	**Fumigation**	**Photosynthesis**	**50% reduction. LOEC.**
3	**Squier *et al.* (1985)**	**Tobacco (*Nicotiana tobaccum* L. cv. Bel W-3). Seedlings.**	**589**	**28 hours**	**Fumigation**	**Photosynthesis**	**70% reduction. LOEC.**
3	**Squier *et al.* (1985)**	**Green ash (*Fraxinus pensylvanica* L.). Seedlings.**	**281**	**28 hours**	**Fumigation**	**Photosynthesis**	**15% reduction. LOEC.**
3	Squier *et al.* (1985)	Corn (*Zea mays* L. cv. F_1 hybrid Early Golden Giant). Seedlings.	112 to 4,600	28 hours	Fumigation	Photosynthesis	No effect at any concentration.
4	**Govindarajan and Poovaiah (1982)**	**Potato (*Solanum tuberosum* L. cv. Russet Burbank). Seedlings.**	**575**	**3 hours**	**Fumigation of attached leaf**	**Photosynthesis**	**10% reduction. LOEC.**
5	**Kays and Pallas (1980)**	**Peanut (*Arachis hypogaea* L. cv. Florunner). 3-wk-old seedlings.**	**288**	**2 hours**	**Fumigation**	**Photosynthesis**	**33% Reduction. LOEC.**
6	**Pallas and Kays (1982)**	**Peanut (*Arachis hypogaea* L. cv. Florunner). 1 to 2 months old.**	**1,150**	**0.25 hours**	**Fumigation**	**Photosynthesis (CO_2 assimilation)**	**Maximum of 27% reduction. Reversible.**
6	**Pallas and Kays (1982)**	**Peanut (*Arachis hypogaea* L. cv. Florunner). 1 to 2 months old.**	**1,150**	**0.5 hours**	**Fumigation**	**Photosynthesis (CO_2 assimilation)**	**Maximum of 34% reduction. Reversible.**
6	**Pallas and Kays (1982)**	**Peanut (*Arachis hypogaea* L. cv. Florunner). 1 to 2 months old.**	**1,150**	**1 hour**	**Fumigation**	**Photosynthesis (CO_2 assimilation)**	**Maximum of 29% reduction. Reversible.**

6	Pallas and Kays (1982)	Peanut (*Arachis hypogaea* L. cv. Florunner). 1 to 2 months old.	1,150	2 hours	Fumigation	Photosynthesis (CO_2 assimilation)	Maximum of 34% reduction. Reversible.
6	Pallas and Kays (1982)	Peanut (*Arachis hypogaea* L. cv. Florunner). 1 to 2 months old.	1,150	4 hours	Fumigation	Photosynthesis (CO_2 assimilation)	Maximum of 48% reduction. Reversible.
6	Pallas and Kays (1982)	Peanut (*Arachis hypogaea* L. cv. Florunner). 1 to 2 months old.	1,150	6 hours	Fumigation	Photosynthesis (CO_2 assimilation)	Maximum of 68% reduction. Reversible.
6	Pallas and Kays (1982)	8 cultivars of peanut (*Arachis hypogaea* L.). 3 to 4 weeks old.	1,150	2.5 hours	Fumigation	Photosynthesis (CO_2 assimilation)	10 to 35% reduction (all significant results).
6	Pallas and Kays (1982)	Jerusalem artichoke (*Helianthus tuberosus* L.).	1,150	2.5 hours	Fumigation of attached leaves	Photosynthesis (CO_2 assimilation)	7% reduction.
6	Pallas and Kays (1982)	Sunflower (*Helianthus annuus* L. line CM90RR).	1,150	2.5 hours	Fumigation of attached leaves	Photosynthesis (CO_2 assimilation)	12% reduction.
6	Pallas and Kays (1982)	Sweet potato (*Ipomoea batatas* L. cv. Red Jewel).	1,150	2.5 hours	Fumigation of attached leaves	Photosynthesis (CO_2 assimilation)	10% reduction.
6	Pallas and Kays (1982)	Bean (*Phaseolus vulgaris* L. cv. Contender).	1,150	2.5 hours	Fumigation of attached leaves	Photosynthesis (CO_2 assimilation)	No effect.
6	Pallas and Kays (1982)	Pea (*Pisum sativum* L. cv. Wando).	1,150	2.5 hours	Fumigation of attached leaves	Photosynthesis (CO_2 assimilation)	No effect.
6	Pallas and Kays (1982)	Irish potato (*Solanum tuberosum* L. cv. LaSota).	1,150	2.5 hours	Fumigation of attached leaves	Photosynthesis (CO_2 assimilation)	No effect.
6	Pallas and Kays (1982)	Sensitive plant (*Mimosa pudica* L.).	1,150	2.5 hours	Fumigation of attached leaves	Photosynthesis (CO_2 assimilation)	No effect.
6	Pallas and Kays (1982)	White clover (*Trifolium repens* L.).	1,150	2.5 hours	Fumigation of attached leaves	Photosynthesis (CO_2 assimilation)	No effect.
6	Pallas and Kays (1982)	Scarlet runner bean (*Phaseolus coccineus* L.).	1,150	2.5 hours	Fumigation of attached leaves	Photosynthesis (CO_2 assimilation)	No effect.
7	Whalen and Feldman (1988)	Corn (*Zea mays* L. cv. Merit). 48-hour-old seedlings.	115	24 hours	In sealed test tubes	Root elongation	Threshold level (significant effect).
8	Crossett and Campbell (1975)	Barley (Hordeum vulgare L. cv. Midas). Germinating seeds.	1,150 to 11,500	7 to 21 days	Bubbled through rooting solution	Root growth	Inhibition of root growth.
9	Jackson *et al.* (1981)	Corn (*Zea mays* L. cv. Limogren 11). 4 leaf stage.	1,150	14 days	Bubbled through hydroponic solution	Root growth	61% reduction at 7 days, 50% reduction at 14 days. LOEC.
10	Lee and LaRue (1992b)	Pea (*Pisum sativum* L. cv. Sparkle).	80	21 days	Forced through rooting medium	Nodulation by *Rhizobium leguminosarum* bv. *viciae* strain 128653	50% reduction. LOEC.
10	Lee and LaRue (1992b)	Sweet clover (*Melilotus alba* cv. U389).	80	21 days	Forced through rooting medium	Nodulation by *Rhizobium meliloti* strain 1021	Near 100% reduction.

	Reference	Plant species	Number	Duration	Treatment	Parameter	Effect
10	Lee and LaRue (1992b)	Soybean (*Glycine max* L. cv. Ransom).	517	21 days	Forced through rooting medium	Nodulation by *Brady-rhizobium japonicum* strain 61A92	No effect.
11	Lee and LaRue (1992a)	Pea (*Pisum sativum* L. cv. Sparkle).	517	3 weeks	Bubbled through rooting solution	*Rhizobium* nodulation; Root growth	94% reduction in nodulation; 40% reduction in growth.
12	Pearce et al. (1992)	Barnyard grass (*Echinochloa oryzoides*). Seedlings.	1,135	3 days	Flow-through chamber	Mesocotyl growth	Mesocotyl shortened by 24%.
12	Pearce et al. (1992)	Barnyard grass (*Echinochloa oryzoides*). Seedlings.	1,135	3 days	Flow-through chamber	Coleoptile growth	No effect.
12	Pearce et al. (1992)	Rice (*Oryza sativa*). Seedlings.	1,135	3 days	Flow-through chamber	Coleoptile growth	Promotion (61%) of growth.
13	Lee and Chu (1992)	Rice (*Oryza sativa*). Seedlings.	1,150	1 to 6 days	Injected into sealed containers	Coleoptile growth and polyamine content	Increase in growth and polyamine content.
14	Woltering et al. (1993)	Carnation (*Dianthus caryophyllus* cv. White Sim). Cut flowers.	173	24 hours	Dark fumigation of cut flowers	Vase life (petal senescence)	Significantly decreased.
14	Woltering et al. (1993)	Carnation (*Dianthus caryophyllus* cv. Chinera). Cut flowers.	265	24 hours	Dark fumigation of cut flowers	Vase life (petal senescence)	Significantly decreased.
14	Woltering et al. (1993)	Carnation (*Dianthus caryophyllus* cv. Epomeo). Cut flowers.	460	24 hours	Dark fumigation of cut flowers	Vase life (petal senescence)	Significantly decreased.
15	Reid et al. (1989)	Rose cv. "Lovely Girl". Cut flowers.	23	2 days	Fumigation of cut flowers	Rate of flower opening	Inhibited by 75%. LOEC. Most sensitive cultivar.
15	Reid et al. (1989)	Rose cv. "Gold Rush". Cut flowers.	≤1,150	2 days	Fumigation of cut flowers	Rate of flower opening	No effect. Most tolerant cultivar.
16	Hanson and Kende (1975)	Morning Glory (*Ipomoea tricolor* Cav.). Excised flowers.	12	7 hours	Dark fumigation of excised rib segments	Rib rolling (senescence)	Increased relative to control. LOEC.
17	Nowak and Fjeld (1993)	*Begonia* (2 cultivars). Mature plants.	173	10 days	Fumigation of whole plant	Flower quality and number	Both significantly decreased.
18	Blankenship et al. (1993)	Easter Lily (*Lilium longiflorum* Thunb. cv Nellie White). Mature plants.	58	77 days	Fumigation of whole plant	Flowering and plant quality (marketability)	Significantly decreased. LOEC.
19	Kays et al. (1975)	Pecan (*Carya illinoensis* [Wang.] K. Koch cv. Desirable).	115	14 days	Fumigation of intact shoots in the field	Shuck dehiscence	Increased. LOEC.
19	Kays et al. (1975)	Pecan (*Carya illinoensis* [Wang.] K. Koch cv. Big Z).	288	14 days	Fumigation of intact shoots in the field	Shuck dehiscence	Increased. LOEC.

	Reference	Species	Conc.	Duration	Method	Measured parameter	Result
20	Goeschl and Kays (1975)	Pea (*Pisum sativum* L. cv. Alaska). Etiolated seedlings.	12	60 hours	Fumigation of seedlings in the dark	Epicotyl and root elongation, epicotyl and root radial expansion, epicotyl and root geotropism	LOEC of 12 µg m^{-3} (10 nl l^{-1}) for inhibition of epicotyl elongation.
20	Goeschl and Kays (1975)	Peanut (*Arachis hypogaea* L., Spanish type, cv. Starr). Etiolated seedlings.	46	60 hours	Fumigation of seedlings in the dark	Epicotyl elongation in rapidly growing seedlings	LOEC of 46 µg m^{-3} (40 nl l^{-1}) for inhibition of epicotyl elongation in rapidly growing seedlings.
20	Goeschl and Kays (1975)	Bean (*Phaseolus vulgaris* L., cv. Burpee's Stringless Green Pod). Etiolated seedlings.	92	60 hours	Fumigation of seedlings in the dark	Epicotyl and root elongation, radial expansion of hypocotyl	LOEC of 92 µg m^{-3} (80 nl l^{-1}) for inhibition of Epicotyl and root elongation, radial expansion of hypocotyl.
20	Goeschl and Kays (1975)	Cotton (*Gossypium hirsutum* L., cv. Stoneville 213). Etiolated seedlings.	368	60 hours	Fumigation of seedlings in the dark	Epicotyl and root elongation, radial expansion of hypocotyl	LOEC of 92 µg m^{-3} (80 nl l^{-1}) for inhibition of Epicotyl and root elongation, radial expansion of hypocotyl.
21	Reid and Watson (1985)	Canola (*Brassica campestris* L. cv. Candle). Whole plant.	0 (ethylene removed)	87 days	Fumigation in sealed chambers	Seed yield	Significantly reduced seed yield relative to a "background" ethylene treatment (12 µg m^{-3}).
21	Reid and Watson (1985)	Canola (*Brassica campestris* L. cv. Candle). Whole plant.	12	87 days	Fumigation in sealed chambers	Seed yield	Seed yield double that in ethylene-free treatment.
21	Reid and Watson (1985)	Canola (*Brassica campestris* L. cv. Candle). Whole plant.	40	87 days	Fumigation in sealed chambers	Seed yield	Seed yield significantly lower (by 63%) than in "background" treatment (12 µg m^{-3}).
21	Reid and Watson (1985)	Oat (*Avena sativa* L. cv. Random). Whole plant.	0 (ethylene removed)	100 days	Fumigation in sealed chambers	Floret number	Floret number significantly higher than "background" ethylene treatment (8 µg m^{-3}).
21	Reid and Watson (1985)	Oat (*Avena sativa* L. cv. Random). Whole plant.	8	100 days	Fumigation in sealed chambers	Floret number	Floret number significantly lower (by 22%) than in ethylene-free treatment.
21	Reid and Watson (1985)	Oat (*Avena sativa* L. cv. Random). Whole plant.	40	100 days	Fumigation in sealed chambers	Floret number	Floret number significantly lower (by 26%) than in "background" treatment (8 µg m^{-3}).
22	Konings and Jackson (1979)	Tomato (*Lycopersicon esculentum* Mill., cv. Moneymaker). Roots.	23	1 day	Fumigation of roots in sealed chambers	Root elongation rate	No effect.
22	Konings and Jackson (1979)	Tomato (*Lycopersicon esculentum* Mill., cv. Moneymaker). Roots.	23	2 days	Fumigation of roots in sealed chambers	Root elongation rate	Root elongation significantly increased relative to control.
22	Konings and Jackson (1979)	Tomato (*Lycopersicon esculentum* Mill., cv. Moneymaker). Roots.	23	3 days	Fumigation of roots in sealed chambers	Root elongation rate	Root elongation significantly increased relative to control.
22	Konings and Jackson (1979)	Tomato (*Lycopersicon esculentum* Mill., cv. Moneymaker). Roots.	23	4 days	Fumigation of roots in sealed chambers	Root elongation rate	Root elongation significantly increased relative to control.

22.	Konings and Jackson (1979)	Tomato (*Lycopersicon esculentum* Mill., cv. diageotropica). Roots.	23	24 hours	Fumigation of roots in sealed chambers	Root elongation	Root elongation significantly increased; at higher levels, elongation significantly decreased.
22.	Konings and Jackson (1979)	Tomato (*Lycopersicon esculentum* Mill., cv. Ailsa Craig). Roots.	23	24 hours	Fumigation of roots in sealed chambers	Root elongation	Root elongation significantly increased; at higher levels, elongation significantly decreased.
22	Konings and Jackson (1979)	Rice (*Oryza sativa* L. cv. IR 20). Roots.	23	24 hours	Fumigation of roots in sealed chambers	Root elongation	Root elongation significantly increased at this and higher concentrations.
22.	Konings and Jackson (1979)	White mustard (*Sinapis alba* L.). Roots.	57.5	24 hours	Fumigation of roots in sealed chambers	Root elongation	Root elongation significantly decreased at this and higher concentrations.
23.	Ageev *et al.* (1996)	Pea (*Pisum sativum* L.). Seedlings.	113.9	48 hours	Fumigation in sealed chamber	CO_2 evolution (respiration) and enzyme (alcohol dehydrogenase) activity	LOEC. Significantly increased CO_2 evolution (respiration), and alcohol dehydrogenase activity relative to control.
23.	Ageev *et al.* (1996)	Pea (*Pisum sativum* L.). Seedlings.	11.39	48 hours	Fumigation in sealed chamber	CO_2 evolution (respiration) and enzyme (alcohol dehydrogenase) activity	Significantly increased CO_2 evolution (respiration), and slightly increased alcohol dehydrogenase activity relative to control.

† LOEC = Lowest Observed Effects Concentration. This is the lowest concentration in a range of concentrations used in the study which induced an effect in the plant.